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NITRATIONS CONFERENCE 1983

Final Report

September 1983

By: D. S. Ross and R. Malhotra

Prepared for:

U.S. ARMY RESEARCH OFFICE
Research Triangle Park, NC 27709

Attention: G. Ronald Husk, Chief
Organic & Polymer Chemistry Branch

Contract DAAG29-83-M-0102

SRI Project PYU-5384

and

U.S. AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling AFB, Bldg. 410
Washington, DC 20332

Attention: Anthony J. Matuszko
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Contract F49620-83-C-0089

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electron transfer	kinetics	electrochemical	
lower nitrogen oxides	mixed acid	polynitroaromatics	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*
In July, 1983, a 2 1/2 day meeting on nitration chemistry was held at SRI International in Menlo Park, CA. The sponsors of the meeting were ARO and AFOSR, and 24 papers on the various aspects of nitration were presented. The 71 attendees heard presentations on the mechanism of aromatic nitration, including discussions of the possible participation of electron transfer, and advanced studies in ipso nitration. Also included were presentations of poly-nitroaromatics and polynitropolyhedranes

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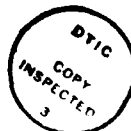Attention: Anthony J. Matuszko
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FOREWORD

Through the cosponsorship of the U.S. Army Research Office, the
U.S. Air Force Office of Scientific Research, and SRI International, the
Nitrations Conference '83 was held at SRI over the period July 27-29,
1983. The 2-1/2-day meeting was structured to include both invited and
submitted papers, and the topics dealt with both the fundamentals of the
mechanism of aromatic nitration and new synthetic procedures for
aromatic and aliphatic nitration. The registered attendance numbered 77
and included visitors from Canada, England, Sweden, and Switzerland.

This report contains a list of all the attendees and abstracts of
all the papers presented at the meeting. Most of the material presented
is current research and will be part of detailed publications in the
near future. In some cases full manuscripts currently under
consideration for publication were provided by the authors.

The chairmen of the meeting would like to acknowledge the actions
of the authors in submitting their material in timely fashion. Their
cooperation and sincere interest in the meeting aided in the development
of the format and were significant factors contributing to the success
of the conference.

We especially acknowledge ARO and AFOSR, and Dr. G. Ronald Husk and
Dr. A. J. Matuszko specifically, for their generous support. This
meeting would not have been possible without the assistance of these
agencies, and the moral support afforded by Dr. Husk and Dr. Matuszko is
particularly appreciated.

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WEDNESDAY, JULY 27

    8:30- 9:00   Registration, Lobby I Building
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    9:05- 9:15   Opening Remarks, Marion E. Hill

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    9:15-10:00   G. A. Olah, University of Southern California
                "RECENT ASPECTS OF AROMATIC NITRATION: NEW
                PREPARATIVE AND MECHANISTIC STUDIES"

    10:00-10:45   J. K. Kochi, Indiana University
                "CHARGE TRANSFER AND ELECTROPHILIC
                AROMATIC SUBSTITUTION"

    10:45-11:15   Coffee Break

    11:15-12:00   J. H. Ridd, University College, London
                "STUDIES OF AROMATIC NITRATION BY ^{15}N NMR
                SPECTROSCOPY"

    12:00-12:45   P. C. Myhre, Harvey Mudd College
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              ACETATE AND 5-CHLORO-2-METHYL-2-NITROCYCLOHEXA-3,5-
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              "NITRATION IN ACETIC ANYHDRIDE: ipso-NITRATION
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2:45: 3:30   R. L. Elsenbaumer, Allied Corportation
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4:20- 4:35   P. Golding, PERME, Waltham Abbey
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11:15-12:00   E. E. Gilbert, US Army ARRADCOM
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12:00-12:05   Concluding Remarks

1:00   Lunch

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RECENT ASPECTS OF NITRATION:
NEW PREPARATIVE METHODS AND MECHANISTIC STUDIES

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New preparative methods of electrophilic nitration and transfer nitration are reviewed, including reactions relating to the ambident reactivity of the nitronium ion. Recent aspects of the mechanism of electrophilic aromatic substitution are discussed.

I.   PREPARATIVE ASPECTS

Nitrations with Nitronium Salts

Nitronium tetrafluoroborate and related nitronium salts are extremely active nitrating agents for aromatics. The nitrations are carried out under anhydrous conditions and therefore substrates which undergo hydrolysis or oxidations in strong acid solutions can be easily nitrated. Aryl nitriles, which could not be dinitrated without hydrolysis, are readily dinitrated with nitronium tetrafluoroborate. Nitronium salts are also effective in nitrating such deactivated substrates as dinitrobenzene.

Alkanes and cycloalkanes give high yields of nitrated products with nitronium salts. Olefins react with nitronium salts in the presence of pyridinium hydrogen fluoride to give vicinal fluoronitroalkanes which can be dehydrofluorinated to give nitroolefins.

$$RCH = CH_2 \xrightarrow[\text{HF-pyridine}]{NO_2^+ \ BF_4^-} RCHFCH_2NO_2 \xrightarrow{-HF} RCH = CHNO_2$$
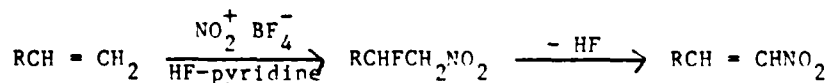
Nitrations with Alkyl Nitrates

In the presence of BF_3 as catalyst, alkyl nitrates provide a particularly mild and selective nitration method,[1] for example, allowing mononitration of durene and other highly alkylated aromatics. Acetone cyanohydrin nitrate has been found to be particularly useful for such nitrations.

Nitrations with Silver Nitrate

$AgNO_3/BF_3$ has been used to nitrate aromatics under heterogeneous conditions. Because of excellent solubility of silver nitrate in acetonitrile, we investigated the nitration of aromatics with $AgNO_3/BF_3$ in acetontrile under homogeneous conditions and found it a useful preparative method. Silver can be recovered from the reaction mixture as the tetrafluoroborate salt.

Nitrations with Solid Superacid Catalysts

Preparative nitrations carried out with butyl nitrate or acetone cyanohydrin nitrate using a perfluorinated resin-sulfonic acid (Nafion-H) provide the cleanest method yet known for aromatic nitrations. All of the byproducts are volatile organic materials and the nitroaromatics can therefore be isolated simply by filtration, without the need for any aqueous basic washing or work-up.[2] Solid superacids can also be used in conjunction with fuming or concentrated nitric acids under conditions of azeotropic removal of water. When the Nafion-H catalyst is modified by impregnating $Hg(NO_3)_2$, the isomer ratio of the product nitroalkylbenzenes show significant differences from conventional acid-catalyzed nitrations, yielding larger amounts of the less hindered isomers.[3]

Transfer Nitrations

Nitrations are usually carried out with acid systems, and an equivalent amount of acid is produced even in nitrations with nitronium salts. When it is required that nitrations be carried out under essentially neutral conditions the acid product must be tied up with a suitable base. This led to the development of transfer nitrations with N-nitropyridinium and N-nitroquinolinium salts. The heterocyclic base, besides binding the acid, also modifies the reactivity of nitronium salts.[4,5]

2

Ambident Reactivity of Nitronium Salts

Nitronium salts were found to react rapidly at -78°C with diaryl, arylalkyl, and dialkyl sulfides affording sulfoxides as the major products. Selenides, phosphines, arsines, and stibines react equally readily giving the oxygenated products. In the case of diphenyl sulfide less than 5% of the ring C-nitro product was formed. These observations suggest the intermediate nitrito onium ion (X^+-ONO) is in equilibrium with the related nitro onium ion (X^+-NO_2). The ambident reactivity of nitronium ion, which was confirmed by a number of spectroscopic studies,[6] has implications in the industrial nitration of aromatics in which phenolic products would arise by attack through the oxygen of the nitronium ion.

Reversibility of Aromatic Nitrations

Nitration is generally considered to be an irreversible reaction, and nitroaromatics, in general, do not undergo rearrangement or isomerization under the reaction conditions; however, some isomerization of the nitro-arenium ion has been observed.[7] We have recently obtained unequivocal evidence for the reversibility of electrophilic aromatic nitration by observing superacid-catalyzed transfer nitration of mesitylene and toluene by 9-nitroanthracene and pentamethylnitrobenzene, respectively, and isolating the product nitromesitylene and nitrotoluens.[8]
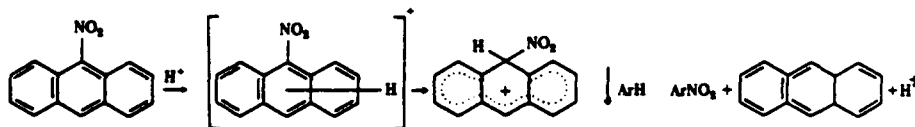
MECHANISTIC ASPECTS

Electrophilic aromatic nitration has been shown by Ingold's classical studies to proceed via the formation of nitronium ion. Reaction of the electrophile with aromatic substrates results in the formation of nitroarenium ions (σ-complex; Wheland intermediate) which, upon proton abstraction, yield the nitro products. A consequence of the two-step one-intermediate mechanism is that substrate and positional selectivities are determined in one and the same step, i.e., the formation of the σ-complex.

3

We found that nitrations with highly reactive nitronium salts under homogeneous conditions results in loss of substrate selectivity (k_T/k_B = 1.7 vs. ca. 20 under normal acidic solutions) with maintenance of positional selectivity (meta substitution <4%). Accordingly, we proposed a three step mechanism in which the first step determines the substrate selectivity (if rate controlling) and the second step, the positional selectivity. Schofield and co-workers similarly found that in nitric acid nitrations in strong acids, substrate selectivity only may be lost, and they also postulated the formation of an intermediate prior to the σ-complex.[9]

The nature of the first intermediate has been discussed by us in terms of π-complex.[10] The fast nitric acid nitrations were interpreted by Schofield and co-workers to be a result of microscopic diffusion control with formation of the first intermediate at the encounter rate, accordingly the name "encounter pair", in which there is no interaction between the reactants. Nitronium salt nitrations have been discussed in terms of macroscopic diffusion control. However, we consider this inadequate to explain many of the experimental observations.

Formulation of the first intermediate in terms of π-complex is strongly supported by the recent observation of a nitronium ion charge transfer complex, reported by Fukuzumi and Kochi between m-tolunitrile and nitronium tetrafluoroborate.[11] The proposal of initial one-electron transfer between the nitronium ion and the aromatic substrate, recently reemphasized by Perrin,[12] resulting in a radical-radical cation pair prior to the formation of the σ-complex is in fact only an extreme of the π-complex formulation. A full one-electron transfer can occur if the ionization potential and electron affinity for the reactants are compatible prior to electronic interactions, and it is named "outer sphere mechanism" in molecular complex terminology.

Our results on the nitration of naphthalene with various nitrating agents in different solvents, as well as other literature data show that the α/β ratio may vary between 9 and 29. Eberson[13] examined the diffusion-controlled radical cation coupling, by reacting solid naphthalene radical cation hexafluorophosphate salt with N_2O_4 and found an α/β ratio of about 40, whereas a ratio of 10-12 was found for the reaction of naphthalene with NO_2BF_4. This addresses the question as to what extent the isomer distribution varies on

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changing the rate limiting step. It is anticipated that the reactivity of the nitrating agent is reflected in the energetics of the first intermediate, affecting the nature and position of the transition state on the reaction corrdinate for σ-complex formation.

REFERENCES

1. Ohah, G. A. and Lin, H. C. (1973) Synthesis, 488-490.

2. Olah, G. A., Malhotra, R. and Narang, S. C. (1978) J. Org. Chem., 43, 4627-4630.

3. Olah, G. A., Krishnamurthy, V. V. and Narang, S. C. (1982) J. Org. Chem., 47, 596-598.

4. Cupas, C. A. and Pearson, R. L. (1968) J. Am. Chem. Soc., 4742-4743.

5. Olah, G. A. Narang, S. C. Olah, J. A. Pearson, R. L. and Cupas, C. A. (1980) J. Am. Chem. Soc. 102, 3507-3510.

6. Olah, G. A. Gupta, B.G.B. and Narang, S. C. (1979) J. Am. Chem. Soc. 101, 5317-5322.

7. Myhre, P. C. (1972) J. Am. Chem. Soc. 94, 7921-7923.

8. Olah, G. A. Narang, S. C., Malhotra, R. and Olah, J. A. (1979) J. Am. Chem. Soc. 101, 1805-1807.

9. Coombes, R. G., Moodie, R. B. and Schofield, K. (1968) J. Chem. Soc. B., 800-804.

10. Olah, G. A. (1971) Acc. Chem. Res. 4, 248-253.

11. Fukuzumi, S. and Kochi, J. K. (1981) J. Am. Chem. Soc. 103, 7240-7252.

12. Perrin, C. L. (1977) J. Am. Chem. Soc. 99, 5516-5518.

13. Eberson, L., Jonsson, L. and Radner, F. (1978) Acta Chem. Scand. B 32, 749-753.

Charge Transfer and Electrophilic Aromatic Substitution

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The transient colors which are often observed during electrophilic aromatic substitutions are attributed to electron donor-acceptor (EDA) complexes of the arenes with a variety of electrophiles. The spectral characteristics of these EDA complexes and others observed in more conventional organic systems will be described, and the electronic transitions presented within the framework of Mulliken charge transfer (CT) theory. Experimental support for the Mulliken formulation based on time-resolved (picosecond) spectroscopic experiments carried out with Hilinski and Rentzepis and with Mataga will be presented.

The relationship between the charge transfer transition energy $h\nu_{CT}$ and the second-order rate constants (log k) for electrophilic aromatic substitution found earlier by Fukuzumi will be summarized. The mechanistic implications of the CT formulation will be presented in the context of inner-sphere electron transfer with a clear distinction made from outer-sphere electron transfer mechanisms.

The kinetics of electrophilic aromatic thallation and mercuration will be described in connection with the associated transient CT spectral changes. The photochemistry of the charge transfer excited states in these systems will be presented, and the ambiguities encountered in directly relating the CT excited state to the activated complex for electrophilic aromatic substitution will be discussed.

Studies of Aromatic Nitration by ^{15}N n.m.r Spectroscopy

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Nitration and a number of related reactions have been followed by ^{15}N n.m.r

spectroscopy using H^{15}NO$_3$ (95% ^{15}N) or ^{15}N labelled substrates. The wide

range of chemical shifts given by ^{15}N n.m.r spectroscopy makes it easy to

distinguish the different products formed and the relatively long relaxation

time of the ^{15}N nucleus facilitates the observation of nuclear polarisation

and thus provides evidence on radical intermediates.

The reactions have been carried out using acetic acid, trifluoroacetic acid

or aqueous sulphuric acid as solvents and the conditions have been adjusted

to give half-lives of ca. 5-10 minutes. The ^{15}N n.m.r spectrum of the

nitrocompounds formed in a number of these nitration reactions then show a

strong emission signal during the course of reaction but this changes to a

conventional absorption signal when reaction is complete. Such observations

are characteristic of nuclear polarisation and point to the formation of

radical pairs at some stage during the reaction.

The substrates giving such spectra include aromatic hydrocarbons with 2 or

more methyl groups, N,N-dimethylaniline (para-nitration only)[1], and

p-nitrophenol. The emission signals appear to derive mainly or completely

from the nitrous acid catalysed component of the reaction. All of these

reactions are susceptible to nitrous acid catalysis and small amounts of

nitrous acid are formed in the course of nitration. For the nitration of

mesitylene, the nitrous acid catalysis and the emission signals are both

absent when a sufficient concentration of nitrous acid scavenger (NaN$_3$) is

added to the nitric acid before reaction. The reactions of p-nitrophenol

include an interesting intramolecular rearrangement of the initial nitro-

group from the para to the ortho-position during the course of reaction to

form 2,4-dinitrophenol. This rearrangement forms about 11% of the total reaction and is presumably initiated by ipso-attack at the para-position. It gives rise to marked nuclear polarisation in the migrating group.

A related reaction showing nuclear polarisation is the nitration of para-methyl-N,N-dimethylaniline by ipso-attack at the C-Me position followed by rearrangement. The two stages of this reaction can be followed separately by [1]H n.m.r spectroscopy: the first is catalysed by nitrous acid but the second is not[2]. When the reaction is followed by [15]N n.m.r spectroscopy, the formation of the ipso-intermediate is accompanied by a large emission signal in the ^{15}N nmr spectrum but nuclear polarisation is not observed during the rearrangement stage. Other reactions showing nuclear polarisation include the rearrangement of [15]NO_2 labelled 2,6-dibromo-N-nitroaniline and N-methyl-N-nitroaniline but these reactions show enhanced absorption in the [15]N n.m.r spectrum for both the starting material and the product[3].

The classical mechanism of nitrous acid catalysed nitration involves electrophilic nitrosation followed by oxidation. On this reaction path, only the oxidation step could give rise to nuclear polarisation and the possibility that this occurs is being investigated. In recent years, there has been increasing evidence for radical intermediates in nitrous acid catalysed nitration and a reaction path involving the radical pair $ArH^{+\cdot}$ $NO_2^{\cdot}$ has also been suggested[2]. The partition of this radical pair between combination and dissociation could then give rise to the nuclear polarisation. Both the emission spectra observed in direct nitration and the enhanced absorption observed in the nitramine rearrangement would then follow from the g-values of the radicals and Kaptein's rules[1,3].

The above work has been carried out in collaboration with Dr J P B Sandall at Bedford and Royal Holloway Colleges in the University of London and much of the work on mesitylene and p-nitrophenol has been carried out by Dr A H Clemens at University College London.

1. J H Ridd and J P B Sandall, Chem.Comm., 1981, 402

2. F Al-Omran et al, J.C.S. Perkin II, 1981, 518

3. J H Ridd and J P B Sandall, Chem.Comm., 1982, 261.

# A Test for Radical Cation-Radical Pairs in Aromatic Nitration?

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The objective of this study is a characterization of the reaction intermediates in nitration of very reactive aromatics. The approach selected was to prepare substances that contained the necessary atoms with nearly the correct constitution and then to allow these substances to undergo molecular reorganization under reaction conditions that would lead to "normal" nitration products. Product, kinetic, and isotopic tracer studies were projected as the means of characterization of the reaction intermediates. Analogous studies have been used earlier to study nitrations of less reactive aromatics.

The present investigation is concerned with formation of nitrophenols. The logical candidates for studies of nitration of phenols by molecular reorganization are 4-alkyl-4-nitrocyclohexadienones, the major first-formed products of nitration of many 4-alkylphenols or 4-alkylphenyl acetates. Previous work by several groups has shown that these nitrodienones undergo rearrangement under a variety of reaction conditions to yield the corresponding 2-nitrophenol.

The nitrodienones shown in Figure 1 have been prepared in connection with this study. In all cases the method of preparation involved low temperature reaction of the phenol or the corresponding phenyl acetate with preformed acetyl nitrate in acetic anhydride solution. Yields range from 40 to 90% depending upon the substitution pattern. The nitrodienones could be purified by low temperature crystallizations, and their structures were deduced from spectral properties.

It has been shown previously that the nitrodienones with a carbon bearing hydrogen adjacent to the ketone function will rearrange in any solvent to yield the 2-nitrophenol derivative, eq 1.

$$(1)$$
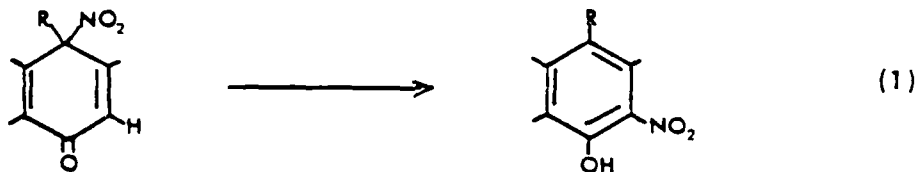
Evidence accumulated previously has lead to the assignment of a radical dissociation recombination pathway for this rearrangement in weakly acidic protic and organic solvents. It has also been shown that this rearrangement is strongly acid catalysed, and it has been inferred from this acid catalysis that the species undergoing rearrangement in strong acid solution is the conjugate acid of the nitrodienone. For many of the nitrodienones shown in

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Figure 1, the product(s) remain the same under "thermal" or acid catalyzed modes of reaction

In addition to a possible concerted rearrangement of the nitro group, at least two modes of reaction involving intermediates could be considered for the acid catalyzed reaction. These are paths that involve dissociation to a paired neutral phenol and nitronium ion, or dissociation into a paired phenol radical cation and nitrogen dioxide. The path to a 2-nitrophenol could then involve collapse of either of these pairs to give the enolizable dienone precursor of the product directly, or separation of the pair followed by subsequent recombination to yield the nitration product.

These two paths involving charged intermediates then represent variants of the path proposed earlier for the rearrangement of nitrodienones in weakly acidic media, a path which has been characterized as one involving formation of a radical pair. It was useful to characterize the thermal reaction by measuring the degree of intramolecularity that attends the rearrangement, and analogous studies have been carried out in acidic solutions. Several kinds of crossover studies have been conducted with the use of labeled samples of 4-methyl-4-nitrocylohexadienone under conditions that favor the the thermal reaction and under conditions of acid catalysis. In all of these studies under thermal conditions (organic or weakly acidic solvents) a substantial intermolecular component is readily detected. The degree of intermolecularity decreases with solvent viscosity, going from approximately 66% in heptane to about 10% in mineral oil. The rate of product formation was only modestly affected by this change in the viscosity of the hydrocarbon solvent.

Corresponding crossover studies with labeled 4-methy-4-nitrocyclohexadienones in the 56 to 96% sulfuric acid range showed less that 2 to 4% of an intramolecular component. These values are considerably lower than those that have been estimated on the basis of deviations of the rate of nitration of phenol from the encounter rate.

While the results of the crossover studies show that the acid catalysed rearrangement of nitrodienones involves a different set of intermediates than the thermal reaction, it is not possible to use the high degree of intramolecularity observed as a means of discriminating clearly among possible concerted, ion/molecule pair, or radical ion/radical pair pathways. In order to pursue this question further, the reaction chemistry of some blocked nitrodienones has been studied. The motivation for this was the thought that with the facile rearrangement of a nitro group to a 2-nitrophenol blocked by methyl subtituents at both the 2-and 6-positions, the product that would eventually form would more effectively report the nature of the key intermediates in the rection.

In chloroform at 25 C, 4-nitro-2,4,6-trimethylcylohexadienone

reacts slowly (half-life = 5.5 hr) to yield 3,5-dimethylnitromethane as the major product together with 1-hydroxy-2,4,6-trimethylcyclohexadienone and a number of more minor side chain substitution products and coupling products. Although the rate of formation of products from this nitrodienone is slow by comparison with structurally related nitrodienones (see rate data shown in Figure 1), the rate at which 4-nitro-2,4,6-trimethylcyclohexadieonone quenches galvanoxyl (taken in excess) is about 1.5 times faster than the rate that 4-methyl-4-nitrocyclohexadienone quenches the same stable radical. The latter rate corresponds well to the rate of formation of 4-methyl-2-nitrophenol from the nitrodienone. The phenylnitromethane product that results from the reaction of an equimolar mixture of nitrogen-15 labeled and carbon-13 labeled 4-nitro-2,4,6-trimethylcyclohexadienone shows complete scrambling of the labels. The conclusion is that this blocked nitrodienone exhibits the characteristics of related nitrodienones in organic solvents, and the rate of product formation is retarded because the radical intermediate in this reaction must find higher barrier reaction channels.

In 85% sulfuric acid, the nitrodienone derived from mesitol yields 2,6-dimethylbenzoquinone, 3-nitro-2,4,6-trimethylphenol and 4-nitro-2,6-dimethylphenol in modest total yield. When the same mixture of nitrogen-15 and carbon-13 labeled nitrodienones (the carbon-13 was at the 4-methyl position) was subjected to reaction in 85% sulfuric acid, no scrambling of label was found in the formal 1,2-shift product, 3-nitro-2,4,6-trimethylphenol. This nitro group migration appears to be entirely intramolecular.

When this blocked nitrodienone was decomposed in 85% sulfuric acid together with a ten-fold excess of mesitylene, the major product was bis-2,4,6-trimethylphenylmethane (40%) together with the abovementioned nitrophenols and benzoquinone plus some uncharacterized high molecular weight products that are believed to be biphenyl derivatives. The use of labeled nitrodienones again revealed no scrambling of labels in the nitration product that forms by a formal 1,2-shift of the nitro group. It is noteworthy that the diphenylmethane derivative contains all of the carbon-13, originally sited at the 4-methyl carbon of the nitrodienone at the methylene carbon.

Possible interpretations of these data and related results will be discussed.
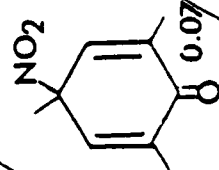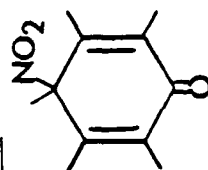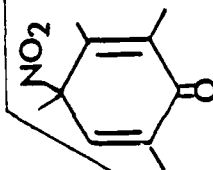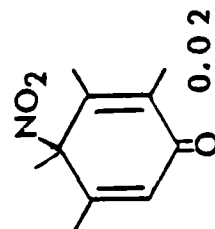
Figure 1
Rates of Thermal Decompostion   ...heptane at 25 C
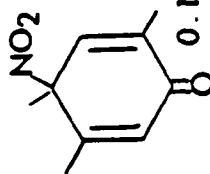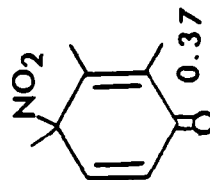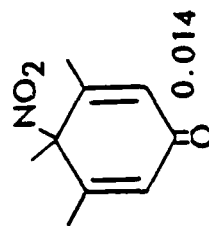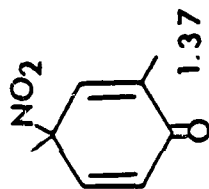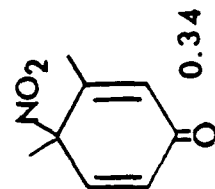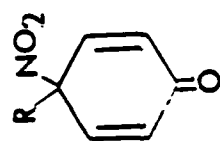
Possible Electron Transfer Steps in Electrophilic Aromatic Nitration

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The hypothesis that nitronium ion can act as an electron
transfer oxidant toward aromatic substrates in the initial step
of electrophilic aromatic substitution has been discussed repeatedly
since 1945 (eqn 1). The product of such a process would be a

$$NO_2^+ \;+\; ArH \;\rightleftharpoons\; \overline{NO_2^{\cdot} \;+\; ArH^{+\cdot}} \qquad (1)$$
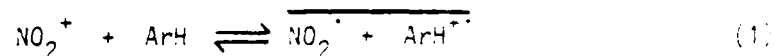
radical-radical cation pair, the components of which would either
undergo recombination to form the usual Wheland intermediate or
diffuse a part to produce products originating from the reaction
between $ArH^{+\cdot}$ and other species present (ArH, solvent) (eqn 2).

$$\overline{ArH^{+\cdot} \; NO_2^{\cdot}} \;\longrightarrow\; \overset{+}{Ar}(H)NO_2$$
$$\big\updownarrow \qquad\qquad\qquad\qquad (2)$$
$$ArH^{+\cdot} \;+\; NO_2^{\cdot}$$
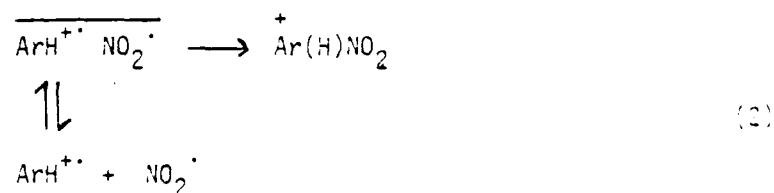
The frequent detection of side-products in aromatic nitration[2]
which formally are products of oxidative substitution (e.g. side-
chain alkoxylation, acyloxylation, acetamidation, and nitrooxylation
of alkylaromatics, biaryl and diphenylmethane coupling, and oxygenation)
indicates great similarity to analogous reactions in anodic[3] and

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metal ion mediated chemistry,[4] many of which must proceed _via_
radical cations.

A modification of this mechanism has been suggested by Ridd[5]
for the nitrous acid catalyzed nitration by NO_2^+ (in trifluoro-
acetic acid) and involves as the crucial electron transfer step
eqn (3), which is then followed by (4) and (5). This interpretation

$$ArH + NO^+ \rightleftharpoons NO^{\cdot} + ArH^{+\cdot} \qquad (3)$$

$$NO^{\cdot} + NO_2^+ \rightleftharpoons NO^+ + NO_2^{\cdot} \qquad (4)$$

$$NO_2^{\cdot} + ArH^{+\cdot} \rightleftharpoons \overset{+}{Ar}(H)NO_2 \qquad (5)$$
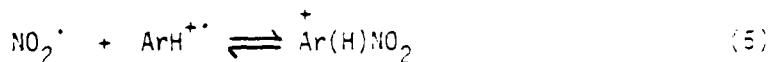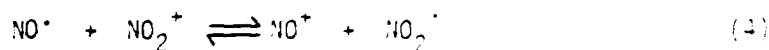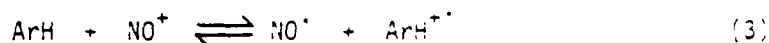
was strongly supported by the observation of C.D.N.P. effects
when $H^{15}NO_3$ was used.

It is the purpose of this paper to discuss the feasibility
of electron transfer steps in aromatic electrophilic nitration,
using the Marcus theory[6] as a starting point, and examine suggested
mechanisms in the light of these results.

RESULTS

The feasibility of electron transfer steps of the types shown
in eqns (1) and (3) can in principle be assessed by the Marcus
theory for non-bonded (a term that for organic systems[7] replaces
the term "outer-sphere" of inorganic chemistry) electron transfer
(ET). According to this treatment, $\Delta G^{\neq}$ for electron transfer between
the two species ArH and NO_2^+ (or NO^+) is given by eqn (6).[9] Here

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$$\Delta G^{\ddagger} = \frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda}\right)^2 \qquad\qquad (6)$$

λ is the <u>reorganization energy</u> (see below) and ΔG^0 the free energy change for ET. The underlying physical model is that of two spherical species, embedded in a continuous medium of dielectric constant D, which diffuse together and form a collision complex within which an electron is exchanged when the transition state has been reached. For the transition state to be reached from the original collision complex, the two reaching species must undergo bond reorganization (bond and/or angle deformations) with a bond reorganization of λ_i, and the immediately surrounding solvent molecules must undergo solvent reorganization (with solvent reorganization energy λ_0) to accommodate electrostatic changes in the transition state upon ET. The reorganization energy of eqn (6), λ, is then the sum of λ_i and λ_0. The need for bond/solvent reorganization to occur before reaching the transition state is a consequence of the Franck-Condon principle, which tells us that transfer of an electron must take place on a time-scale (<u>ca</u> 10^{-16} s) which is much faster than that of nuclear movements (10^{-13} s).

For any electron transfer reaction Marcus' theory demands that λ can be expressed as the mean value of the λ values of the two corresponding self-exchange reactions. For the ET process of eqn (1), the self-exchange reactions are shown in eqns (7) and (8).

$$\mathrm{ArH^{+\bullet}} + \mathrm{ArH} \rightleftharpoons \mathrm{ArH} + \mathrm{ArH^{-\bullet}} \qquad\qquad (7)$$

$$\mathrm{NO_2^+} + \mathrm{NO_2^{\bullet}} \rightleftharpoons \mathrm{NO_2^{\bullet}} + \mathrm{NO_2^+} \qquad\qquad (8)$$

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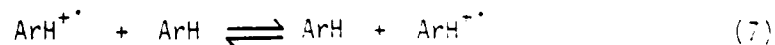
Values of λ for self-exchange reactions can be experimentally determined (for a list, see Ref. 8).

In order to estimate ΔG° of eqn (1), one needs E° of $ArH^{+\cdot}/ArH$ and $NO_2^{+}/NO_2^{\cdot}$. The latter value was obtained from Bontempelli et al.[10] (1.56 V),[11] whereas E° for oxidation of aromatic hydrocarbons have been determined by Parker.[12] Values of λ for $ArH^{+\cdot}/ArH$ self-exchange reactions are not known, but from available generalizations about λ and a consideration of the corresponding $ArH/ArH^{-\cdot}$ processes,[8] it can be safely concluded that they are ≤ 10 kcal mol^{-1}. For the NO_2^{+}/NO_2 reaction a value of ≤ 20 kcal mol^{-1} was estimated; the cyclic voltammogram of the NO_2^{+}/NO_2 couple is nearly reversible,[10] indicating a fast self-exchange process.

The other species of interest, NO^{+}, has an E° of 1.51 V[10] and on the same ground as above the λ value of the NO^{+}/NO self-exchange reaction can be estimated to be ≤ 20 kcal mol^{-1}.

With these starting parameters, λ of eqns (1) and (3) will be $\leq 1/2 \, (10 + 20) = 15$ kcal mol^{-1}, and this value was used in the calculation to be described below. A variation of ± 1 kcal mol^{-1} in λ at $\Delta G^{\circ} \sim 20$ kcal mol^{-1} corresponds to a change in the calculated log $\underline{k}$ value of ± 0.2 log units, showing that this parameter is not the crucial one in determining the rate constant.

Calculations according to eqn (6) were performed for a ΔG° interval between -15 and +25 kcal mol^{-1}. Instead of reporting $\Delta G^{\ddagger}$, log $\underline{k}$ values were calculated by the Eyring equation (log $\underline{k}$ = 10^{11} exp $(-\Delta G^{\ddagger}/RT)$ for the simple kinetic scheme of eqn (9)[12]

$$ArH + NO_2 \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [ArH \; NO_2^{+}] \xrightarrow{k_{el}} ArH^{+\cdot} + NO_2 \quad (9)$$

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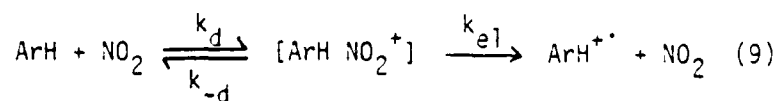
where k_d was taken to be 10^{10} M^{-1} s^{-1}.

These results are given in Table 1, together with those for some real cases of interest for the discussion (benzene, toluene, naphthalene, mesitylene, hexamethylbenzene, dibenzo-1,4-dioxin, anthracene, perylene, Zn(II)tetraphenylporphyrin, ferrocene).

Looking first at the lower part of Table 1, rate constants are seen to approach the diffusion controlled value at $\Delta G^O < -5$ kcal mol^{-1}. In terms of the real cases listed in the upper part of the Table, this means that compounds with E^O values equal to or lower than that of perylene (1.30 V) are predicted to react with electron transfer with NO^+ or NO_2^+ at diffusion controlled rates (these reagents are so similar in oxidation potential that for all practical purposes they can be considered equivalent in this respect). This does however not tell us that such reactions do proceed via ET; they may follow the usual type of heterolytic mechanism and only experimental studies will decide between these mechanistic alternative.

On the other hand, for reactions with $\Delta G^O > 5$ kcal mol^{-1}, electron transfer can be ruled out in the case of nitronium ion, since reactions have experimentally been shown to proceed at diffusion controlled rates. Suggested ET steps in nitration and nitrosation reactions will be discussed from this point of view.

References

1. For leading references, see a) C.L. Perrin, J. Am. Chem. Soc.
   99 (1977) 5516; b) L. Eberson, L. Jönsson and F. Radner, Acta
   Chem. Scand. B 32 (1978) 749; c) L. Eberson and F. Radner, Ibid.
   B 34 (1980) 739.

2. For a review, see H. Suzuki, Synthesis (1977) 217.

3. For reviews, see L. Eberson and K. Nyberg, Acc. Chem. Res. 6
   (1973) 106; Adv. Phys. Org. Chem. 12 (1976) 1.

4. R.A. Sheldon and J.K. Kochi, Metal-Catalyzed Oxidations of
   Organic Compounds, Academic Press, New York, 1981.

5. A.H. Clemens, J.H. Ridd, and J.P.B. Sandall, J. Chem. Soc. Chem.
   Commun. In press; F. Al-Omran, K. Fujiwara, J.C. Giffrey, J.H.
   Ridd and S.R. Robinson, J. Chem. Soc. Perkin II (1981) 518.

6. R.A. Marcus, Ann. Rev. Phys. Chem. 15 (1964) 155.

7. J.S. Littler, in Essays on Free-Radical Chemistry, Special
   Publications No. 24, Chemical Society, London (1970) 383.

8. For a review on ET in organic chemistry, see L. Eberson,
   Adv. Phys. Org. Chem. 18 (1982) 79.

9. Actually the complete expression contains terms expressing
   the influence of electrostatic interactions, but these can be
   neglected in the cases under discussion (reaction between
   neutral molecule and singly charged ion).

10. G. Bontempelli, G.A. Mazzocchin and F. Magno, J. Electroanal.
    Chem. 55 (1974) 91.

11. All potentials given refer to the normal hydrogen electrode.

12. V.D. Parker, J. Am. Chem. Soc. 98 (1976) 98.

13. See Ref. 8, eqn. 70.

14. H. Siegerman, in Technique of Electroorganic Synthesis (N.L.
    Weinberg, ed.), Part II, Wiley, New York, p. 673.

Table 1. Calculated log $\underline{k}$ (M^{-1} s^{-1}) for ET reactions between ArH and $NO^+(NO_2^+)$.

Compound (E^0/V)[a]	ΔG^0/kcal mol^{-1} [b]	log $\underline{k}$ (M^{-1} s^{-1}) for reaction with	
		NO^+	NO_2^+
Benzene (3.03)	35.0, 33.8	-19.9	-18.4
Toluene (2.61)	25.4, 24.2	-9.2	-8.1
Mesitylene (2.43)	21.2, 20.0	-5.5	-4.3
Naphthalene (2.08)	13.1, 11.9	1.1	1.9
Hexamethylbenzene (1.85)	7.8, 6.6	4.3	5.0
Dibenzo-1,4-dioxin (1.7)	4.4, 3.2	6.1	6.7
Anthracene (1.61)	2.3, 1.1	7.0	7.5
Perylene (1.30)	-4.8, -6.0	9.3	9.5
Zn(II) TPP (0.95)	-12.9, -14.1	9.9	9.9
Ferrocene (0.60)	-21.0, -22.2	9.8	9.7
	25		-8.9
	23		-6.9
	21		-5.1
	19		-3.4
	17		-1.8
	15		-.3
	13		1.1
	11		2.4
	9		3.7
	7		4.8
	5		5.8
	3		6.7
	1		7.6
	-1		8.3
	-3		8.9
	-5		9.4
	-7		9.7
	-9		9.8
	-11		9.9
	-13		9.9
	-15		9.9

[a] E^0 values were taken from Ref. 8 or 14. [b] The first number refers to the NO^+ reaction, the second one to the NO_2^+ reaction.

ELECTRON TRANSFER AND LOWER NITROGEN OXIDES

IN AROMATIC NITRATION

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The accepted mechanism for aromatic nitration in mineral acid media includes the acid promoted, rapid and reversible formation of nitronium ion from nitric acid, followed by electrophilic attack of the ion on the aromatic substrate. This scheme is considered to be operative over a very wide acidity, covering the range 40-96% sulfuric acid.

Our studies have been concerned with a number of aspects of nitration mechanism, including the possible roles of electron transfer and lower nitrogen oxide chemistry in the process. In particular we have focused on the question of the chemistry taking place in the 55-75% H_2SO_4 range, where reactive substrates such as phenol and naphthalene undergo a catalyzed nitration brought about by the accumulation of lower nitrogen oxides. Considerable work has been reported on the nature of the catalysis, and we shall present some of our own work in that area below. However we have focused on the very initial chemistry, that responsible for the generation of the lower oxides, as well as identification of the specific lower oxides present. The research performed on our program has included ion molecule studies in a high pressure mass spectrometer, and a detailed look at the effects of N(III) (nitrite, nitrous acid, and nitrosonium ion) in nitration under conditions where no prior nitrosation takes place.

N/O Species in Sulfuric Acid. Initially it was of interest to determine what N/O species are dominant over various acidity ranges. The species we are dealing with cover the common nitrogen oxidation states: N(II)/NO; N(III)/noted above; N(IV)/NO_2, N_2O_4; and N(V)/nitrate, nitric acid, nitronium ion. The prevalent species are of course a function of acidity, and even at 25°C, any one oxidation state can yield several others. The rate of disproportionation of N(IV) is rapid at room temperature, and we have found it convenient to use this reaction as an entry into the equilibrium positions of several of
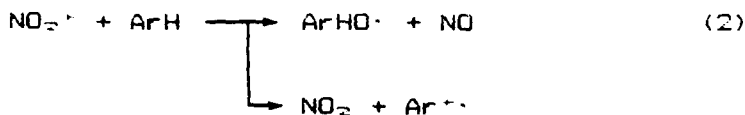
the N/O species over the full range of sulfuric acid acidities.
Experiments were conducted in which both the condensed and vapor
phase species were determined quantitatively. The study was
carried out both in the presence and absence of oxygen, in a
reactor containing 50 ml of liquid phase and 170 ml vapor phase,
and with an initial charge of 100 torr of NO_2 in each case.

It is recognized that N(IV) as N_2O_4 rapidly
proceeds to NO^+ and NO_2^+ in sulfuric acid at
acidities greater than about 93%. We began our study there, and
proceeded systematically to lower acidities. As expected from
the literature (Deno, et al., 1961), N(V) became fully nitric
acid at about 85% sulfuric acid, and its ionization to nitrate
began at 60% acid. In 20% sulfuric acid, nitrate was virtually
fully formed.

Nitrosonium ion also behaved as expected from literature
accounts (Bayliss, et al., 1963), and was converted to nitrous
acid, beginning at 70% acid. Nitrous acid is a relatively weak
acid ($pK_a=3.4$), and so nitrite appeared in the pH range.
Nitrous acid itself disproportionates, however, and so from 60%
H_2SO_4 down, quantities of NO appeared in the gas phase.
The system becomes rather complicated below 60% acid, so that for
example at 30% sulfuric acid for the O_2-free case, the
prevalent species and their mole percents were HNO_3, 7%; NO,
20%; HONO, 28%; nitrate, 45%.

The most complex region in the study for the O_2-free
case was in 55-65% acid, where not only were several of the
condensed phase species present (HNO_3, NO_3^-,
NO^+, HONO), but both NO and NO_2 were prominent in the
vapor phase. The presence of NO_2 was suprising, since its
full disproportionation would be expected at any acidity. While
the concentrations of these gas phase species in the acid phase
could be very low under nitration conditions, their possible
roles in nitration must be considered.

Ion Molecule Study. The potential presence of NO_2
in reaction media suggested that an electron transfer route to
nitration could be considered, and accordingly an ion molecule
study at 10 torr in a high pressure mass spectrometer was carried
out. The findings for aromatic substrates including benzene,
toluene and p-xylene were

$$NO_2 + ArH^{+\cdot} \longrightarrow ArHNO_2^{+} \qquad (1)$$

$$NO_2^{+} + ArH \longrightarrow ArHO\cdot + NO \qquad (2)$$
$$\longrightarrow NO_2 + Ar^{+\cdot}$$

Thus the odd electron system in eq. 1, involving the radical cation of the aromatic substrate, leads to the Wheland intermediate for aromatic substitution. The even electron system in eq. 2, isoelectronic to the system in eq. 1 and representing the conventional nitration scheme, leads only to oxygen or electron transfer. No evidence for the sigma-bonded Wheland intermediate was found for this case.

The direct application of this finding to chemistry in the condensed phase may be suspect, but clearly the conventional nitronium ion scheme can be questioned on the basis of the fact that the direct reaction of an aromatic substrate with nitronium ion at least initially leads to O- rather than N-attachment.

Electron Transfer. Once the possibility of radical cation intermediates in nitration arises, the oxidant in the system must be considered. It is recognized of course that nitric acid is a good oxidant; it is also known that the oxidizing power of nitric acid increases with increasing acidity (Latimer, 1952). However less well known is the finding by Vetter (1950) that the electron acceptor in nitric acid is NO_2, via an acid catalyzed process. With this chemistry we can suggest the following nitration sequence, a proposed alternative to the nitronium ion scheme.

$$H^{+} + NO_2 + ArH \longrightarrow ArH^{+\cdot} + HONO \qquad (3)$$

$$ArH^{+\cdot} + NO_2 \longrightarrow ArHNO_2^{+} \qquad (4)$$

$$HONO + HNO_3 \longrightarrow 2NO_2 + H_2O \qquad (5)$$

This sequence provides the net stoichiometry, and at least qualitatively the acid catalysis, observed for nitration in acid media. Additionally, it predicts that nitration should be promoted by the lower nitrogen oxides through chemistry not

involving prior nitrosation of the aromatic substrate.

      <u>Lower Nitrogen Oxides and Nitration.</u> The accepted view
of lower nitrogen oxide promoted nitration is one including prior
nitrosation of the substrate, followed by oxidation of the
nitroso group. Recently however, work by Giffney and Ridd
(1979), Main, Moodie and Schofield (1982), and our group (1980)
showed that nitrosation is not necessary, at least for some
substrates. Our work dealt with the nitration of phenol in 56%
sulfuric acid, and showed that while nitrosation/oxidation of
phenol was a part of the nitration, a significant nitration
component was operative involving lower nitrogen oxides
catalysis, but no prior nitrosation. The specific nature of the
catalysis was not developed in our account.

      Present work with hydrocarbon substrates in place of phenol
has advanced the understanding, and has shown that naphthalene
undergoes lower oxide catalysis of nitration under conditions
where no nitrosation takes place. The research includes a
kinetic study in 56% sulfuric acid, in which the initial rates of
nitration are determined. No lower nitrogen oxide scavangers
such as urea are used, and each run is performed in fresh acid,
to which aliquotes of the substrate and then aqueous sodium
nitrate and sodium nitrite solutions are added. We have
established that at the spectrophotometric concentration levels
of the study, the substrate is fully soluble in the medium. The
use of nitrate and nitrite salts insures that at least initially,
no lower nitrogen oxides are present. Also, in recording the
initial rates, we are able to cover in the study any chemistry
dealing with the initial oxidation/reduction processes important
to the nitration.

      We have found that the nitration is cleanly 3/2 order in
naphthalene, a result in mixed acid nitration without precedent
to our knowledge. This finding extends to other runs carried out
for which the kinetics were followed beyond the initial rates to
>3 half-lives. The orders in N(V) and added N(III) are 0-1,
depending on the N(V) concentration, and 0.8 respectively.

      The electron transfer schemes discussed by both Giffney and
Ridd, and Main, Moodie and Schofield, include 1-electron
oxidation of the aromatic substrate by NO$^+$. And the scheme
we have suggested above includes NO$_2$ as the oxidant.
However none of these schemes are consistent with a 3/2 order in
aromatic substrate. We have considered that the fractional order
might be explained by a chain process, but we presently have no
fully suitable model for the finding. We feel that this lower
oxide catalyzed nitration is important to mixed acid nitration in
general, and our investigations are continuing.

A COMPUTATIONAL STUDY OF INTERMEDIATE STAGES IN THE INTERACTION OF
NO_2^+ WITH BENZENE AND TOLUENE.

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ABSTRACT

We have investigated intermediate stages in the interaction of NO_2^+
with benzene and with toluene, using an ab initio self-consistent-field
molecular orbital procedure. In each case, we found evidence of a weakly-
bound complex in which the ion is located above the aromatic system, as
well as a relatively strongly-bound product which can be described as a
sigma complex:
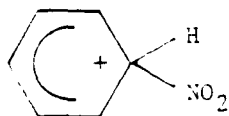
The structures, energies, and atomic charge distributions in these systems
will be discussed.

A B S T R A C T

Title: Can mixing processes influence the regioselectivity
         in aromatic nitrations ?

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Abstract: It is well established that the substrate selectivity
          in nitrations can be influenced by mixing. Conditions
          shall be discussed under which mixing processes can
          also disguise the intrinsic positional selectivity.

THERMAL HAZARDS EVALUATION
OF AROMATIC NITRATION WITH NITRIC ACID

Abstract

Both isothermal and adiabatic aromatic nitrations with aqueous nitric acid have been practiced industrially with mixed success. The thermal hazards posed by these processes are formidable. Through the use of adiabatic calorimetry, the thermal hazards of nitric acid nitration may be better defined. In addition, valuable information regarding the thermodynamics and kinetics of the aromatic nitration may also be obtained.

The conditions of nitrobenzene process which suffered a major explosion were simulated in an accelerating rate calorimeter (CSI-ARC). Under the feed ratios employed in this process, the adiabatic temperature rise during the benzene nitration was sufficient to effect subsequent dinitration even though the molar concentration of nitric acid was quite low. The heat release during dinitration was then found to be sufficient to raise the temperature of the system to the deflagration point.

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LASER POWERED HOMOGENEOUS PYROLYSIS OF NITROAROMATICS

## THE MECHANISM OF HOMOGENEOUS, GAS-PHASE DECOMPOSITION OF NITROTOLUENES

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Laser Powered Homogeneous Pyrolysis (LPHP) has been used to characterize the initial step(s) in the homogeneous thermal decomposition of ortho-nitro-toluene. In this technique an absorbing, but unreactive, gas (eg. SF_6) is heated by a pulsed infrared laser. The hot SF_6 then transfers its thermal energy by collision to the substrate. The heat transfer and reaction take place on a time scale which is very short compared to diffusion times. Therefore, reaction takes place remote from the walls and only within the region swept by the laser beam. This technique thus provides conditions in which ortho-substituted nitro-toluenes have no opportunity to undergo wall-catalyzed reactions. If, under these conditions, the "abnormal" rate parameters and products commonly reported for gas phase decomposition of the ortho isomers are not observed, then we will begin to have a baseline for understanding the interactions between the methyl group and adjacent nitrogroups that are evidently important in condensed phase decomposition.

"NORMAL" DECOMPOSITION

$$\log k = 17.1 - 69/2.3 \; RT$$

ABNORMAL DECOMPOSITION

$$\log k = 12.4 - 49.5/2.3 \; RT$$
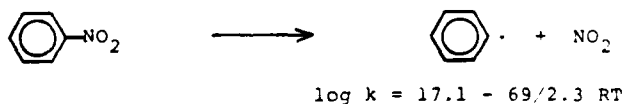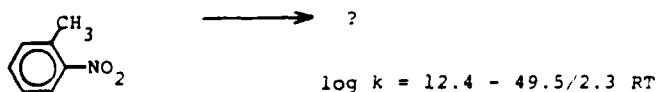
Matveev et al., Izv. Akad. Nauk., Ser. Khim., 2, 479 (1978)

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In fact, preliminary measurements of o-nitrotoluene decomposition rates indicate an activation energy 66 kcal/mole, in line with the ca. 70 kcal/mole "normally" expected for $Ph-NO_2$ bond scission. Similarly, the principal decomposition product of ortho-nitrotoluene (>95%) under these conditions was toluene, as expected if phenyl-NO_2 bond scission was the initial decomposition step, and the methyl-phenyl radical was effectively scavenged. The implications that these "normal" rate parameters and products have for the origin of the commonly observed "abnormal" decomposition will be discussed.

Mechanisms of Two Nitration Reactions: p-Substituted

Anisoles, and Trichlorodinitrobenzene

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Introduction

This paper is concerned with the importance of *ipso*-attack[1] in nitration in two cases, coming from opposite ends of the spectrum of aromatic reactivity. Nitration of p-substituted anisoles, reactions which occur at or close to the encounter rate between aromatic and NO_2^+, give rise to nitrophenols as well as nitroanisoles.[2] Thus (1a) gives a mixture of (2a) and (4a),[3] and (1c) behaves similarly.[4] The phenolic products arise from *ipso*-attack, demethoxylation to give the dienone intermediate (3) in equilibrium with its conjugate acid, and rearrangement (Scheme 1). In order to gain more information about this reaction, and particularly about the rearrangement step (3) → (4), we studied the kinetics and products of nitration in aqueous sulphuric acid of the anisoles (1a-f) and of the corresponding phenols (5a-f).

The dienone (3a) has been shown to rearrange to the nitrophenol (4a) in a number of solvents by a radical mechanism.[5] A change in mechanism with increasing acidity is indicated by the onset of acid catalysis at the acidity represented by 60% H_2SO_4.[6,7] This acid-catalysed reaction might occur as in Scheme 2 through dissociation of the conjugate acid of the

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dienone into a solvent-caged pair (e.p.) of the phenol (5) and nitronium ion. It is possible to estimate approximately the extent of leakage from such a pair (which is the same as the encounter pair formed in the nitration of (5)) because it is related to the closeness of the rate coefficient for nitration of (5) to the rate coefficient for an encounter controlled nitration in the same medium.[8,9] The extent of leakage is measurable because it leads to the formation of (5) in the nitration of (1), either as an intermediate (when nitric acid is taken in excess) or as a product (when the anisole (1) is taken in excess and can act as a scavenger for nitronium ion formed through leakage). Taken together, these observations can therefore lead to an estimate of the fraction of the rearrangement of the dienone (3) which takes place *via* the nitronium ion/phenol encounter pair. Such studies are described in this paper.

The nitration of trichlorodinitrobenzene, which requires oleum at 150 $^{\circ}$C, gives tetrachlorodinitrobenzene along with the expected trichloro-trinitrobenzene. The former is thought to arise following *ipso*-attack at nitro, capture, decomposition of the diene, and liberation of chlorine which is in, or is oxidised to, a form suitable for chlorination of starting material.

Results

Kinetics.- Second order rate constants for nitration of the reactive aromatics are compared with those for nitration of mesitylene, an encounter controlled reaction, in the Table. In the nitration of (1ab) and (5ab) dienone intermediates were detectable spectroscopically. Rate coefficients for further reaction of these intermediates are compared in the figure.

Products.- These were determined for each substrate under a range of conditions, and will be reported.

Discussion

We discuss first the evidence concerning the mechanism for the rearrangement of the dienone (3). In Scheme 2 a mechanism is put forward in which the dienone proceeds *via* its conjugate acid to the encounter pair (e.p.) of substituted phenol (5) and nitronium ion. The encounter pair may "leak" to give (5), or produce the nitrophenol (4). Kinetic analysis permits an estimate to be made of the extent of the leakage.

The conventional experimental second-order rate coefficient for the nitration of phenol (5) is defined by k_2^5obs. = Rate/[5][HNO_3]. A similar definition applies for each of the coefficients k_2^1obs. and k_2^Mobs., relating to the anisole (1) and to mesitylene, respectively. The nitration of mesitylene is thought to be entirely encounter-controlled.[8]

The fraction, f, of the encounter pair which leaks is related to the closeness of the rate constant for the nitration of (5) to the rate constant for encounter-controlled nitration in the same medium. If the nitration of (5) were wholly encounter-controlled then there would be no leakage (f=0). Otherwise, and assuming that the rate constants for the diffusion steps, (5) meets nitronium ion and mesitylene meets nitronium ion, are equal, then f is given by equation (1).

$$f = 1 - (k_2^5 \text{obs.}/k_2^M \text{obs.})$$ (1)

Application of the steady-state approximation to [3] and [e.p.] in Scheme 2 shows that f is defined by equation (2).

$$f = k_s/[k_s + k_r + \{k'k_z/(k' + k_z)\}]$$ (2)

In Scheme 2 the fraction of (3) which gives (5) is the product fg, in which f is the quantity defined above, and $g = k_{-2}/(k' + k_{-z})$ is the fraction of (3)

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taking the encounter pathway. The product f_g can be evaluated from equations (3) and (4) which again follow from application of the steady-state approximation.

$$f_g = Y_5^\infty / (Y_5^\infty + Y_4^\infty)$$ (3)

$$f_g = \left(\frac{Y_5^t}{Y_4^\infty}\right)\left(\frac{k_2^5 obs. - k_2^1 obs.}{k_2^1 obs.}\right)\left(e^{-k_2^1 obs.[HNO_3]t} - e^{-k_2^5 obs.[HNO_3]t}\right)^{-1}$$ (4)

Y_5^∞ and Y_4^∞ are yields of (5) and (4) at the end of the reaction, and Y_5^t is the yield of (5) at time t. Equation (3) applies when aromatic is taken in excess over nitric acid (preventing the freed phenol from being nitrated), and equation (4) applies when nitric acid is taken in excess.

If it be acknowledged that diffusion-rate constants for different aromatics meeting nitronium ion vary over a small range, and if a factor of 2 be adopted to cover the range of values, we can modify equation (1) to give a minimum value of f, as in equation (5).

$$f_{min} = 1 - 2(k_2^5 obs. / k_2^M obs.)$$ (5)

Values of f_g, f, and f_{min}, with the consequent values of g and g_{max} are in table. That g_{max} is most often less than unity justifies the inclusion of the step with rate constant k' in Scheme 2.

The significant points, as they relate to the individual species, are these. For (3a) g_{max} is 1, which suggests that (3a) may proceed to (4a) entirely by the encounter pair route. Such leakage as there is may arise because p-cresol is not quite reactive enough to react entirely upon

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encounter, a surprising conclusion which has been discussed
before and attributed to hydrogen bonding.[4,6]   The same can be said of
dienone (3b) rearranging in 76.4% H_2SO_4, because g_{max} is 1.   However in
69.2% H_2SO_4, g_{max} for (3b) is only 0.26:   thus not more than $ca.$ a quarter
of the reaction of (3b) takes place through the encounter pair;   the alternative
k' pathway predominates.   Reference to the rate profile for this rearrangement
(Fig. 1) suggests that the results could be explained satisfactorily if the
k' pathway is the non-acid catalysed reaction observed at low acidities,
and the acid catalysed decomposition takes place, largely though not
necessarily completely, through the encounter pair route.   If the above
conclusions apply also to the dienone (3c) formed from 4-chloroanisole (1c),
an increase in g with increasing acidity might be expected.   There is some
indication that this happens (Table)   but the uncertainties arising from
small yields and long reaction times preclude firm conclusions.   It is
clear however that the encounter pair pathway accounts for less than half the
rearrangement at all acidities studied.

Dienones formed from (1d) and (1e) give no detectable yields of phenols;
less than 2% of each of these reactions proceeds via the encounter pair.

The effects of medium and substituents on the fraction g ($i.e.$
on the relative importance of the encounter pair, as opposed to the k'
pathway) can now be summarised.   g Increases with acidity;   2-chloro
substituents reduce g (compare (1a) with (1b), and (1c) with (1d), in
Table 10).   g Decreases as the 4-substituent is changed from methyl to
chloro to fluoro (compare (1a), (1c) and (1e) in Table).

Our results give little information on the nature of the k' pathway,
but by analogy with the conclusions of previous workers on similar reactions,[5,1]
a radical mechanism seems likely.   The observation that nitration of (5e)
(a reaction which proceeds entirely by the k' pathway) leads to the formation

of a small amount of 2-(4-fluorophenoxy)-4-fluorophenol is in accord

with such a conclusion, for the "dimer" could arise from the reaction

of the 4-fluorophenoxy radical with 4-fluorophenol. An alternative

source of 2-(4-fluorophenoxy)-4-fluorophenol would be the reaction

with 4-fluorophenol of 4-fluorophenoxenium ion, formed by loss of

nitrite ion from (3e). However such a reaction would be expected to

give also the products of C-C coupling.[11] Heterolysis of (3) in this

way would be favoured by electron releasing substituents, yet the

reverse is true for k'. These two observations argue against the

alternative view that the k' pathway proceeds by nitrite loss from

(3). Our view is then that the k' pathway probably involves

formation of a solvent caged, aryloxyradical-nitrogen dioxide pair,

from which there can be some leakage. The possibility arises that

the free aryloxy radical can then be reduced to the phenol. There is

no evidence for this, and in any case it would not alter the status

of g_{max} in the forgoing discussion.

Unlike the similar rearrangement (6) → (7),[10] (3e) → (4e) is not

rate limited by proton loss, as   product isotope effects

testify. This is in accord with the suggestion[12] that steric hindrance

from the NMe_2 group is to some extent responsible for proton loss

being rate determining in (6) → (7).

The rearrangement of (5d) gives no leakage and therefore proceeds

by the k' pathway. The products from reaction of (1d) include

2,4-dichloro-5-nitrophenol (the yield of which increases with increasing

acidity) but no 2,4-dichloro-5-nitrophenol.   Scheme 4 accounts

for these observations. The 2,4-dichloro-5-nitroanisole is seen to

arise from the ipso-Wheland intermediate (8) formed at C-4, by 1,2-

migration of the nitro-group (path 3). This process, together with reversal by loss of nitronium ion (path b) competes more effectively with demethoxylation mediated by water (path f) as the acidity increases. (The very low yield of 2,4-dichloro-5-nitroanisole at low acidities suggests that direct nitration at C-5 (path d) is insignificant). It is noteworthy that (8) gives the products of both formal 1,2- and 1,3-migration, but (3d) gives only that of 1,3-migration. This contrast suggests that the k' pathway is not acid catalysed, for protonated (3d) is closely similar in structure to (8).

Nitration of (9) in oleum at 150 $^\circ$C follows a rate law which is first-order in the concentration of nitric acid and of (9). It gives a mixture of (10) and (11). The initial ratio of yields (10) : (11) increases from 50:50 in 98% H_2SO_4 to 90:10 in oleum containing 29% excess SO_3 by weight (29% oleum). The products, particularly (11), are unstable at the lower acidities but in > 11% oleum their stabilities are sufficient to establish that the overall yield based on chlorine in the starting materials and products is quantitative within experimental error.

These and the following observations cast light on the mechanism by which the unexpected product (11) is formed.

A. Addition of (10) at the start of the reaction has no effect on the kinetics or products of reaction of (9). This excludes (10) as either the donor or recipient of the transferred chlorine; the latter must come from (9) and react with (9).

B. Addition of m-dinitrobenzene markedly diminishes the relative yield of (3), and chlorodinitrobenzenes can be detected amongst the products. This indicates that there is formed from (9) an electrophilic chlorinating agent. Since there is a "chlorine balance" at the end of the reaction, each molecule of (9) which decomposes must give up all of its chlorine in this way.

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C.   If nitration of (9) is effected with $H^{15}NO_3$, both (11) and remaining (9), extracted after ca. 2 half-lives for nitration, are found to contain ^{15}N.   Enrichments of (9) were 0.8% (2.8% oleum) 4.8% (18.7% oleum) 5.8% (28.0% oleum).

On the basis of all this information we advance the incomplete mechanism shown in Scheme 5.   (9) Reacts with NO_2^+, either at the unsubstituted position to give (10) or ipso to the nitro group to give, reversibly, an ipso-Wheland intermediate.   This can be captured by an unidentified nucleophilic species X (perhaps HSO_4^-) to give a diene.   The partitioning of the Wheland intermediate, between return to starting material and nucleophilic capture, moves in favour of the latter as acidity decreases, thus decreasing the extent of ^{15}N-incorporation and increasing the relative yield of (11).

The way in which the diene decomposes is unclear, but it is suggested that under the vigorous conditions decomposition is complete and yields, perhaps after oxidation by nitric acid, 3 moles per mole of an electrophilic chlorinating agent which we loosely identified as "Cl^+" in the scheme. These then react with (9) to form (11).

The experiments with $H^{15}NO_3$ provide the first identification of ipso-attack at a $C-NO_2$ position, and of the process of nitro-denitration.

REFERENCES

[1] R.B. Moodie, and K. Schofield, *Acc. Chem. Res.*, 1976, *9*, 287.

[2] K. Schofield, *Aromatic Nitration*, Cambridge University Press, 1980, p. 195.

[3] J.W. Barnett, R.B. Moodie, K. Schofield, J B. Weston, R.G. Coombes, J.G. Golding, and G.D. Tobin, *J. Chem. Soc., Perkin Trans. II*, 1977, 248.

[4] R.B. Moodie, K. Schofield, and G.D. Tobin, *J. Chem. Soc., Chem. Comm.*, 1978, 180.

[5] C.E. Barnes, and P.C. Myhre, *J. Amer. Chem. Soc.*, 1978, *100*, 973.

[6] R.G. Coombes, J.G. Golding, and P. Hadjigeorgiu, *J. Chem. Soc., Perkin Trans. II*, 1979, 1451.

[7] R.G. Coombes, unpublished work.

[8] R.G. Coombes, R.B. Moodie, and K. Schofield, *J. Chem. Soc. B*, 1968, 800.

[9] H.W. Gibbs, L. Main, R.B. Moodie, and K. Schofield, *J. Chem. Soc., Perkin Trans. II*, 1981, 848.

[10] F. Al-Omran, K. Fujiwara, J.C. Giffney, J.H. Ridd, and S.R. Robinson, *J. Chem. Soc., Perkin Trans. II*, 1981, 518.

[11] R.A. Abramovitch, G. Alvernhe, R. Bartnik, N.L. Dassanayake, M.N. Inbasekaran, and S. Kato, *J. Amer. Chem. Soc.*, 1981, *103*, 4558.

[12] J.H. Ridd, private communication.

Partitioning in the rearrangement in Scheme 2

| Aromatic	H_2SO_4 (%)	fg[a]	k_2^5obs./k_2^Mobs.[b]	f	f_{min}[c]	g	g_{max}
1a	64.5	0.21[d]	0.56	0.44	(0.21)	0.48	1
	67.1	0.20[d]	0.56	0.44	(0.20)	0.48	1
1b	69.2	0.14[d]	0.23	0.77	0.54	0.18	0.26
	76.4	0.15[d]	ca.15	ca. 0	(0.15)	ca. 1	1
1c	61.5	0.17[e]	0.19	0.81	0.62	0.21	0.27
	63.7	0.25[d]	0.19	0.81	0.62	0.31	0.40
	63.7	0.20[e]	0.19	0.81	0.62	0.25	0.32
	66.1	0.21[d]	0.21	0.79	0.59	0.27	0.36
	66.2	0.23[e]	0.21	0.79	0.59	0.29	0.39
	67.3	0.24[e]	0.21	0.79	0.59	0.30	0.41
	70.0	0.23[d]	0.24	0.76	0.52	0.30	0.44
1d	64.5	<0.01[d,f]	0.02	0.98	0.96	<0.01	0.01
1e	67.1	<0.01[d,f]	0.22	0.78	0.56	<0.01	0.02
	73.7	<0.01[d,f]	0.26	0.74	0.47	<0.01	0.02

[a] For definitions of f and g, see text.   [b] For definitions see text.

[c] Figures in parentheses result from the constraint $g \leqslant 1$.   Otherwise values are obtained as described in the text.   [d] From equation 3.   [e] From equation 4.
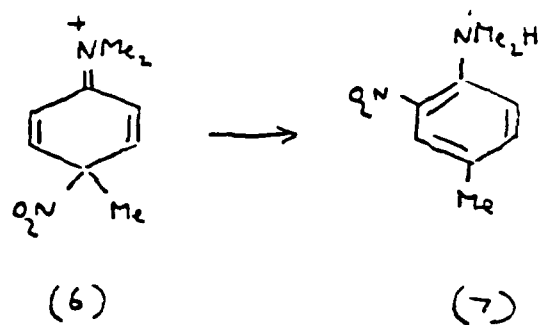
[f] Based on the estimate that >0.2% of (5) would have been detected.   [g] By extrapolation of rate data for (5b).
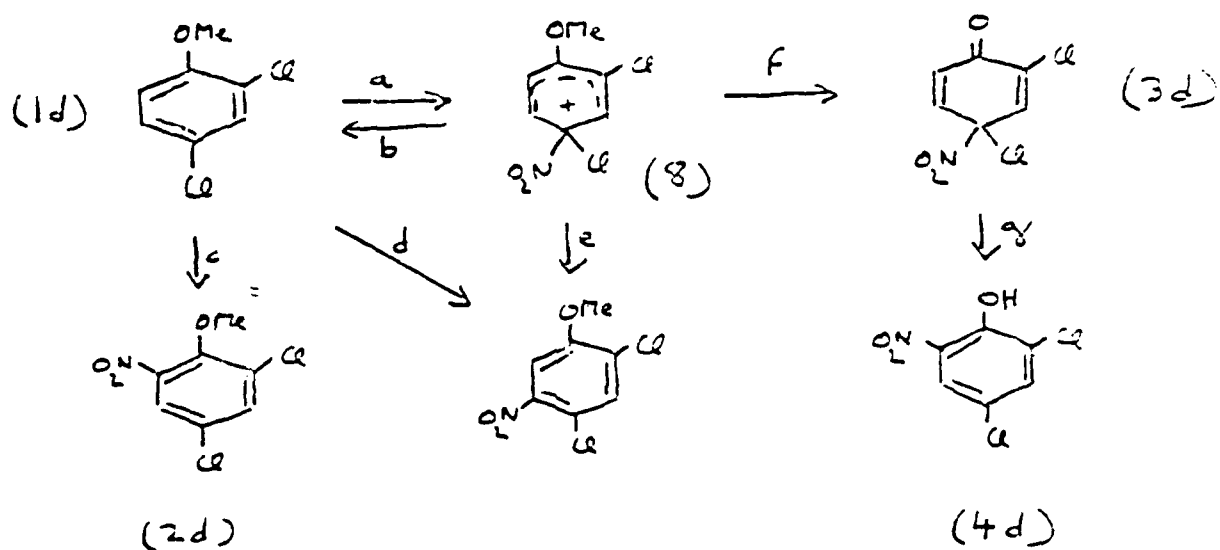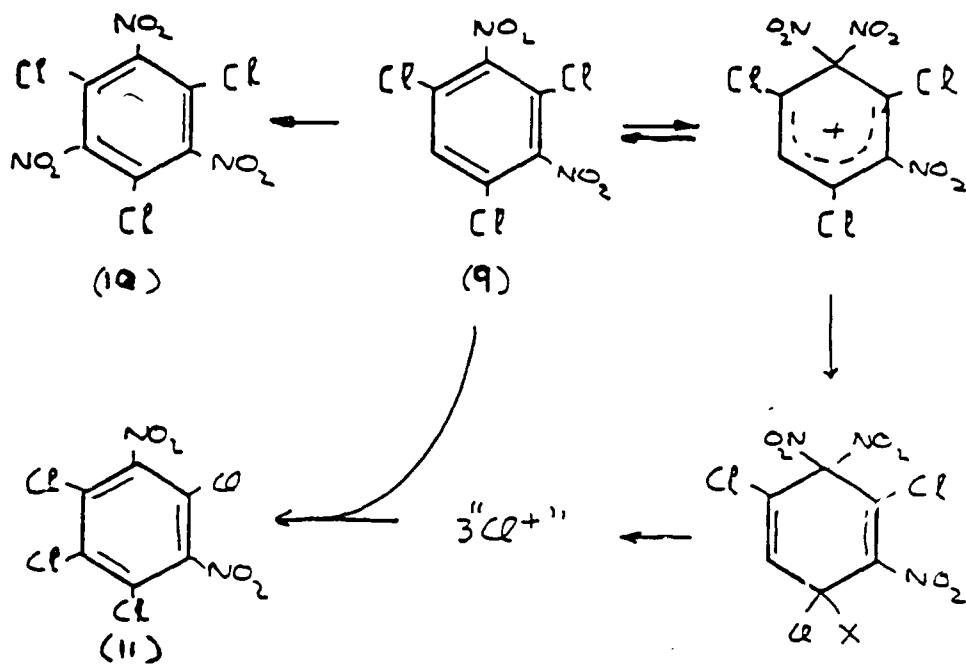
Scheme 1

Scheme 2

41
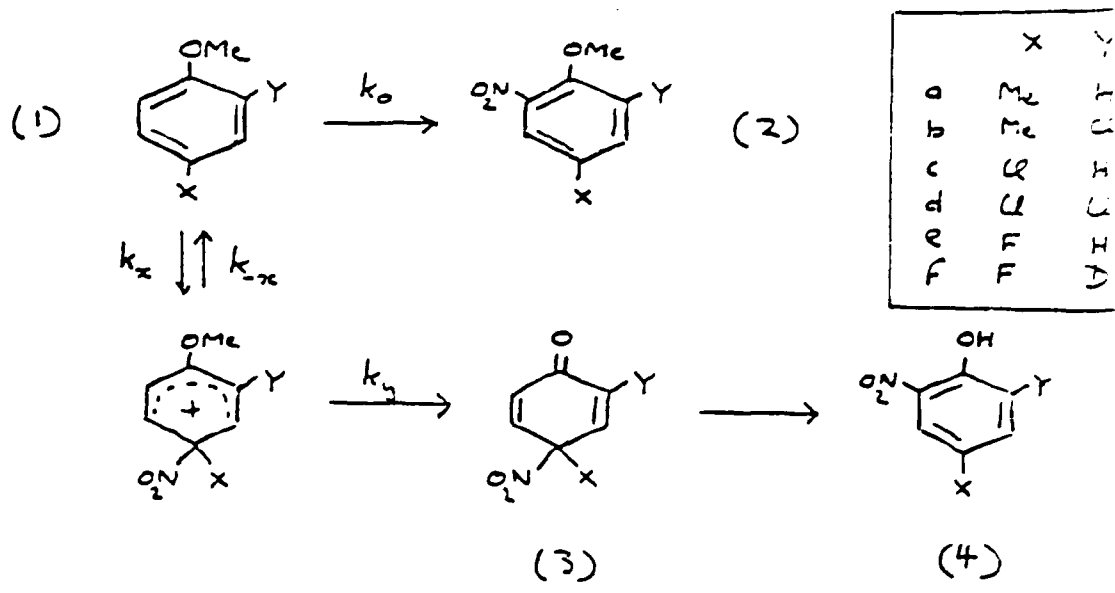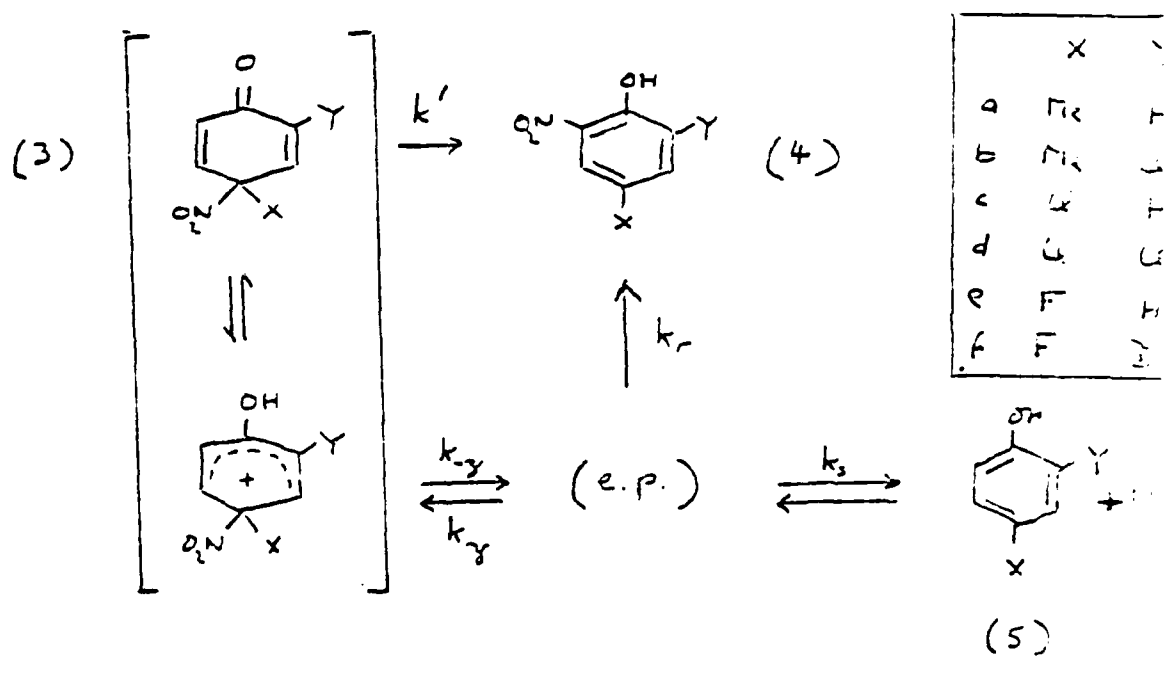
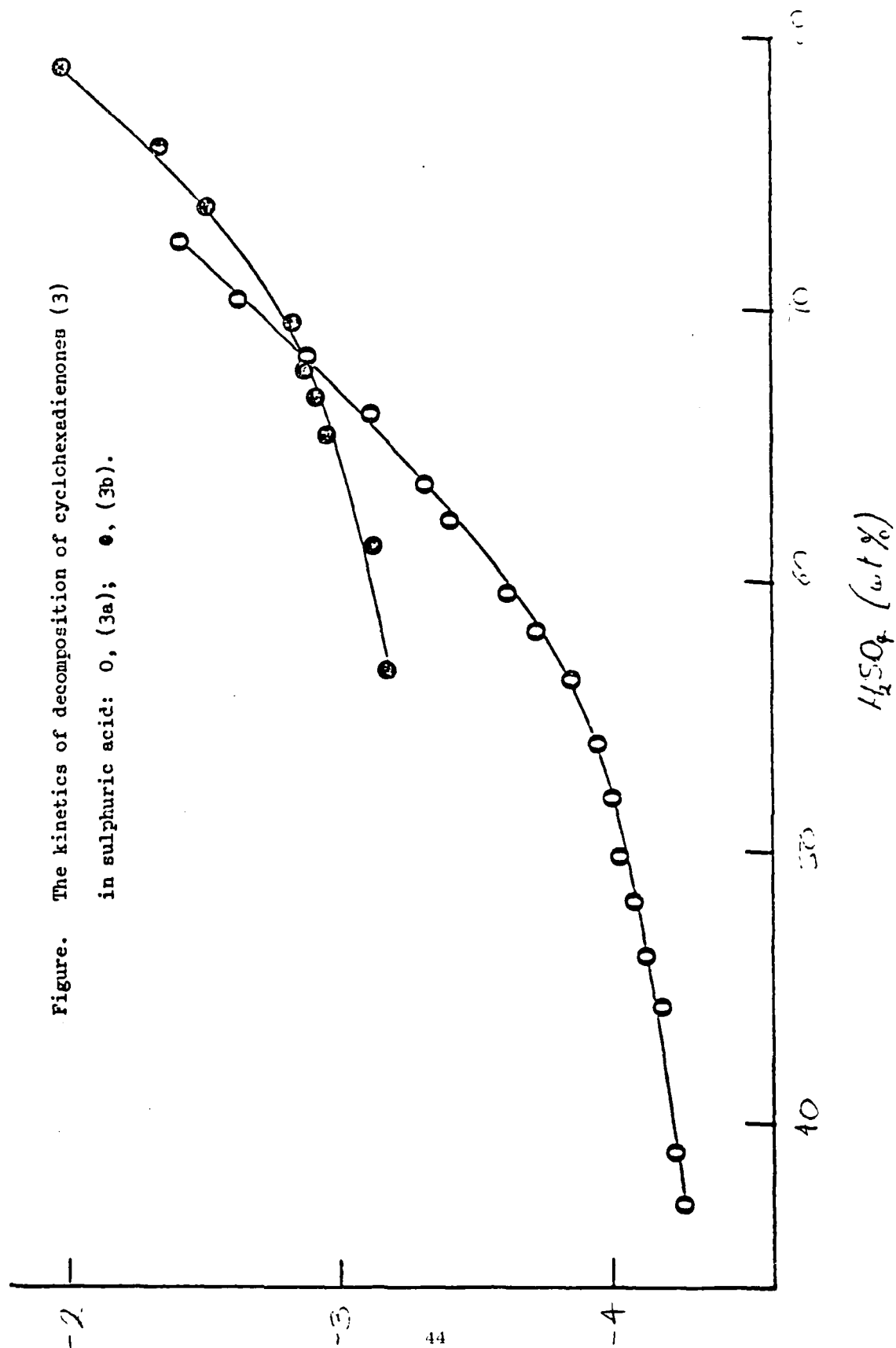Scheme 3

Scheme 4

scheme 5

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Figure. The kinetics of decomposition of cyclohexadienones (3) in sulphuric acid: O, (3a); ●, (3b).

The Kinetics and Reactions in Sulphuric Acid of 2-Cyano-3,4-dimethyl-4-
nitrocyclohexa-2,5-dienyl Acetate and 5-Chloro-2-methyl-2-nitrocyclohexa-
3,5-dienyl Acetate, and their respective Relationships to the Nitrations
of 2,3-Dimethylbenzonitrile and 4-Chlorotoluene

By C. Bloomfield, R.B. Moodie, and K. Schofield

The occurrence of *ipso*-attack in aromatic nitration has several
consequences which complicate the outcome of the reaction, and in particular
obscure the nature of the primary processes involved. A valuable method
for elucidating these complications is that introduced by Myhre,[1] which
consists in generating *ipso*-Wheland intermediates, $(W_i$'s), independently
of nitrations, by acid solvolysis of the nitro-acetates isolable from
nitrations in acetic anhydride. These nitro-acetates react in several ways
in addition to the $A_{AL}1$ solvolysis which generates the W_i, and these are
themselves, as reactions of a product of nitration, relevant to nitration
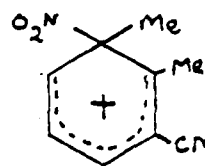processes in general.

This paper is concerned with the two nitro-acetates (1)[2] and (2).[3]
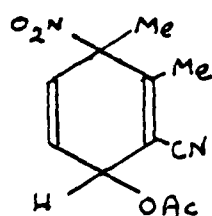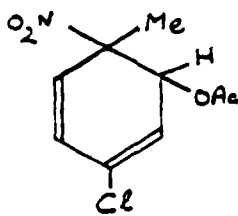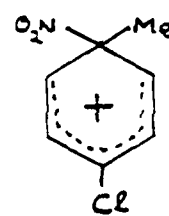

(1)   (2)   (3)   (4)

The generation from (1) of 2,3-dimethyl-5-nitrobenzonitrile has been
regarded[2] as an intramolecular 1,3-rearrangement proceeding *via* the W_i (3).
Such a reaction would have important implications, and was difficult to accept.

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Accordingly, the reactions of (1) in 61.8 - 79.5% sulphuric acid have been studied quantitatively; it proved possible to study not only the products, but also the kinetics of the reactions. Concurrent elimination of nitrous acid and the $A_{AL}1$ generation of (3) occur. (3) Reacts by intermolecular rearrangement (as shown by the isolation of 2,3-dimethylbenzonitrile and the trapping of nitronium ion by reaction with 4-fluorophenol), by nucleophilic capture by water, and by intramolecular 1,2-rearrangement to 2,3-dimethyl-4-nitrobenzonitrile. The results permit the demonstration that the solvolysis of (1) which generates (3) is indeed an $A_{AL}1$ reaction, as is proved by the dependence of its rate upon acidity, and also that the elimination of nitrous acid from (1) is acid-catalysed. The solvolytic reactions of (1) do not lead to intramolecular 1,3-rearrangement of the nitro-group, and the formation of 2,3-dimethyl-5-nitrobenzonitrile from (1) under non-solvolytic conditions appears to be a thermal reaction of (1).[4]

Combination of the solvolysis results with those for the nitration of 2,3-dimethylbenzonitrile in 70.4 - 82.5% sulphuric acid show that the major primary consequence of the nitration is *ipso*-attack.

For (2) the kinetics of reaction in water and in 6.5 - 43.6% sulphuric acid at 25.0 °C (higher acidities could be reached at 5.0 °C), and products formed in water and 6.5 - 92.4% sulphuric acid, were measured. (2) Reacts by three mechanisms, all acid-catalysed; nitrous acid elimination, and $A_{Ac}2$ and $A_{AL}1$ solvolyses. With increasing acidity the solvolyses gain in importance, and above about 45% sulphuric acid the $A_{AL}1$ is increasingly dominant. The W_i (4) reacts by nucleophilic 1,2-capture by water, by reversion to 4-chlorotoluene, and by 1,2-rearrangement to 4-chloro-2-nitrotoluene; these fates, as they depend on acidity, have been quantitatively evaluated.

Combination of the solvolysis results with those for the nitration of

4-chlorotoluene[5] permit the evaluation of the extent of primary attack by nitronium ion at the C-Me position. It is higher than the minimum extent previously suggested,[5] and more in line with the implication from the high yield of (2) obtained by nitrating 4-chlorotoluene in acetic anhydride.[3] In fact, it is likely that overall *ipso*-attack is the major primary reaction of nitronium ion with 4-chlorotoluene, but the extent of it occurring at C-Cl is not known.

References

[1] P.C. Myhre, *J. Amer. Chem. Soc.*, 1972, *94*, 7921.

[2] A. Fischer and C.C. Greig, *J.C.S. Chem. Comm.*, 1973, 396; *Can. J. Chem.*, 1974, *52*, 1231.

[3] A. Fischer, D.L. Fyles, and G.N. Henderson, *J.C.S. Chem. Comm.*, 1980, 513.

[4] Professor A. Fischer regards this and related reactions which he has discovered as sigmatropic rearrangements (Private communication).

[5] R.B. Moodie, K. Schofield, and J.B. Weston, *J.C.S. Perkin II*, 1976, 1089.

Nitration in Acetic Anhydride: ipso-Nitration and its Consequences

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Aromatic nitration involves in its initial step the addition of a nitronium ion to a nuclear carbon to generate a nitrocyclohexadienyl cation. In the past decade it has become evident that the nitronium ion readily adds to a substituted nuclear carbon, a process described as *ipso* addition. Generally, the resulting cyclohexadienyl cation does not lose the original substituent and it is constrained to undergo reactions other than that resulting in substitution. The most conspicuous of these is the addition of a nucleophile to form a cyclohexadiene derivative, which occurs in the course of nitration in acetic anhydride.
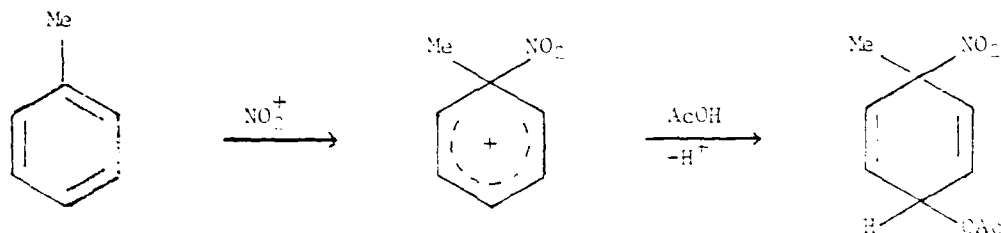
Competition between *ipso*-nitration and nitration at an unsubstituted position, and therefore between addition in substitution, is controlled by the relative reactivity of the substituted and unsubstituted position(s). In the case of toluene only a few percent of the adduct is obtained indicating that the *ipso* position is less reactive than the *m-* or *p-* position. In *ortho-* or *para-*xylene introduction of the second methyl group greatly increases the reactivity of the *ipso* position relative to the unsubstituted positions (in addition to the statistical factor) and adduct becomes the major product. As illustrated, 1,4-adducts are normally obtained. However, some substrates give 1,2-adducts, e.g.,
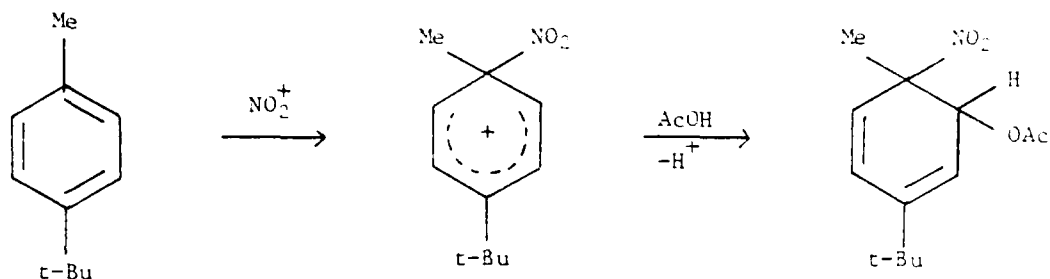
The nitrocyclohexadienyl acetate adducts are reactive species. An adduct readily reverts to the nitrocyclohexadienyl cation by acid-catalysed loss of the acetate. The cation can reform the same or a different adduct by capture of a nucleophile. In strongly acid conditions it is less susceptible to such reaction and it can then undergo migration of the nitro group and formation of a nitroarene.
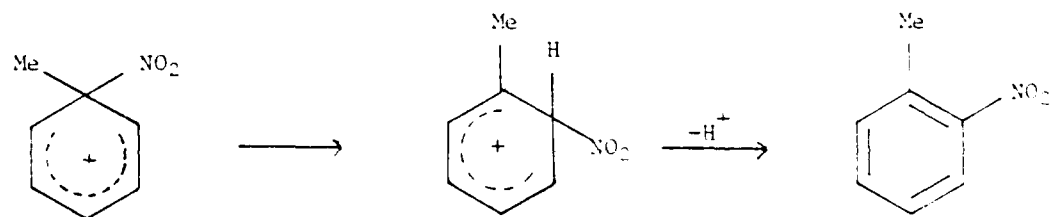
This reaction occurs when nitration is carried out in the usual strongly acidic conditions and thus the products of ipso-addition are not observed.

A competing reaction of the adduct which is favoured in less acidic and more strongly ionizing conditions is solvolysis of the nitro group to form an acetoxycyclohexadienyl cation, e.g.,
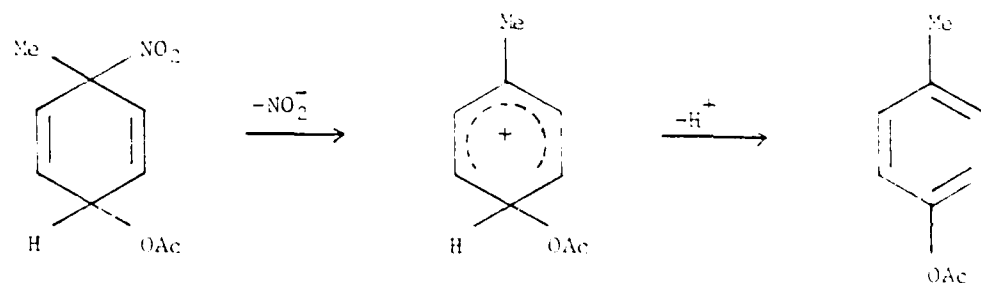
It has recently been observed that 1,2-adducts undergo a $\begin{bmatrix} 1,5 \end{bmatrix}$ sigma-tropic nitro-shift, e.g.,
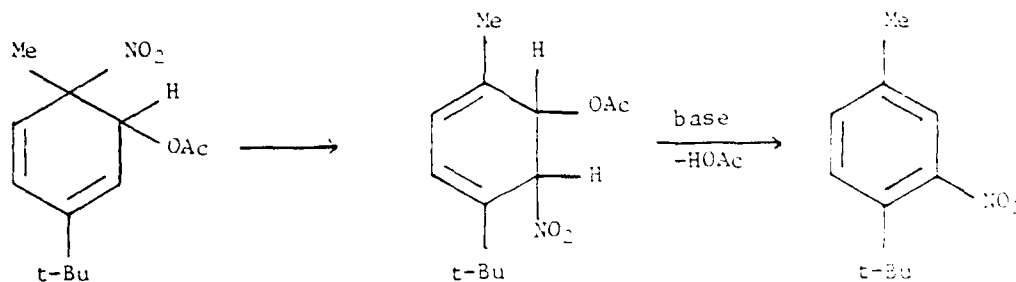
As indicated the rearranged adduct readily eliminates acetic acid on treatment with a base and forms, in the illustrated case, 3-nitro-4-t-butyltoluene. Direct nitration of 4-t-butyltoluene did not give this nitroarene. A non-stereospecific pathway for the rearrangement also exists and provides a route to the enantiomer of the original 1,2-adduct as well as both enantiomers of the rearranged adduct.

ISOMER DISTRIBUTION IN MIXED ACID NITRATION OF TOLUENE

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Mononitration of toluene with nitric acid in sulfuric acid between 0 and 100 deg. C is widely documented to yield approximately 60% o-, 5% m- and 35% p-nitrotoluenes. For practical reasons these results represent only a narrow range of sulfuric acid concentration. Below 30 mole% sulfuric, reaction is extremely slow, and above 33-35 mole% sulfuric, reaction is so fast that significant if not complete dinitration occurs. To circumvent the problem of overnitration the variation of isomer distribution obtained upon dinitration of o- and m-nitrotoluenes has been measured from 30 mole% to 90 mole% sulfuric at various levels of nitric acid. These results permit the distributions of dinitrotoluenes obtained as higher acid concentrations to be corrected to give the isomer compositions of the intermediate mononitrotoluenes. At high acid strengths the content of m-nitro-toluene drops as low as 1.5% and the o/p ratio as low as 1.1. The problem of slow reaction at low acid strength has been solved for a few points by the application of patience.

The assumptions involved in this treatment will be discussed.

Since selectivity has increased as the palpable measures of reactivity have increased, the usual selectivity-reactivity relationships clearly do not apply. The rates of mixed acid toluene mononitrations have been shown by Strachan to be mass transfer limited, and additional data demonstrating this phenonmenon will be presented. The variations of selectivity with acid strength are proposed to result from mass transfer effect(s).

POLYMERIC NITRATING AGENTS

by

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Merrifield pioneered the field of solid phase synthesis
more than two decades ago. Since then, a large number of
polymeric reagents have been prepared for numerous synthetic
applications. Polymeric nitrating agents, however, have not
received much attention from both preparative and mechanis-
tic points of view. The following benefits can be expected
when polymeric supports are used as reagents for nitration.
(i) Ease of Processing. This as the most important con-
sideration as work-up and purification of resulting nitro
compound is reduced to simple filtration followed by
evaporation of the solvent.

This advantage alone is sufficient to justify.the
use of polymeric reagents in nitrations. But there are
other advantages to their use. (ii) Polymer Recovery
Regeneration: A properly designed polymeric nitrating
agent will allow one to recover the spent polymer quantita-
tively. Furthermore, such a reagent could be regenerated
in a simple manner without any appreciable loss of activity.

(iii). <u>Ease of Handling</u>: Odorless polymeric reagents
of reduced toxicity can be prepared whose monomeric analogs
are associated with significant toxicity and/or noxious odors.

(IV). <u>Influence of Polymer Backbone and Microenvironment.</u>
The reactivity of the polymeric reagent may be modified
considerably compared to the monomeric system because of the
steric electronic influence of the backbone. Also, the
local environment around the polymer bound reagent may be
different because of possible differences in solvation.
The reaction kinetics would thus be affected.

(V). <u>Mechanistic Probes:</u> Use of polymeric analogs of
monomeric nitrating agents may help to answer some of the
questions about the mechanism of nitration with these reagents.

Based on these possible advantages, the following
polymeric nitrating agents have been synthesized.

I   II

$-H_2C-N-CH_2-$

III

X^-

IV

V

X^-

$$-\overset{\overset{\displaystyle NO_2}{|}}{S^+}-(CH_2)_x-S-(CH_2)_x-\overset{\overset{\displaystyle NO_2}{|}}{S^+}-(CH_2)_x-$$

VI

$X^- = BF_4^-,\ PF_6^-,\ AsF_6^-$ etc.

$-CH-CH_2-$

$C = O$

$O-NO_2$

VII

$-CH_2-CH-$

$C = O$

$O-NO_2$

VIII

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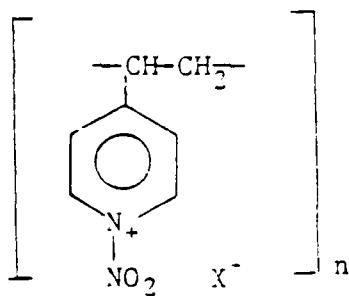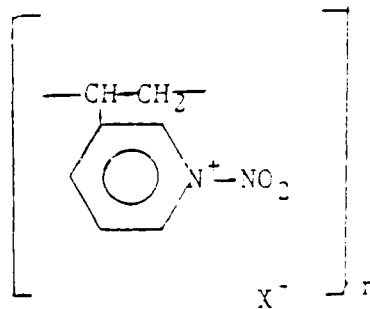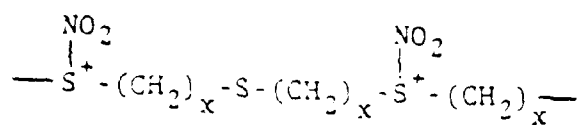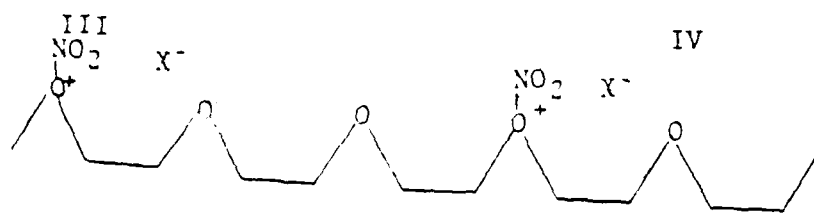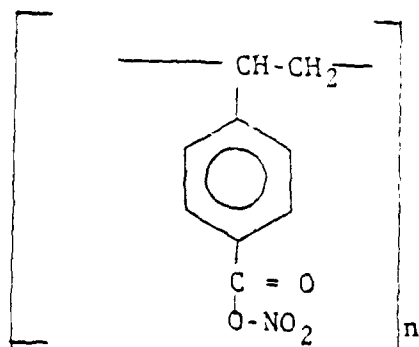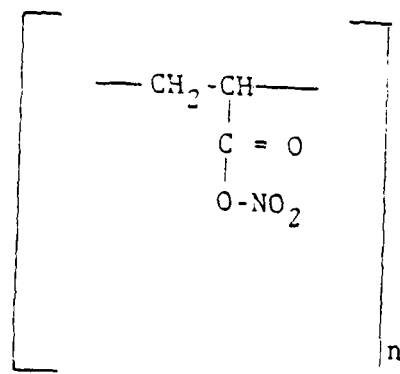
Polymer I and II have been synthesized by reaction of poly(4-vinylpyridine) and poly(2-vinylpyridine) with nitronium salts.
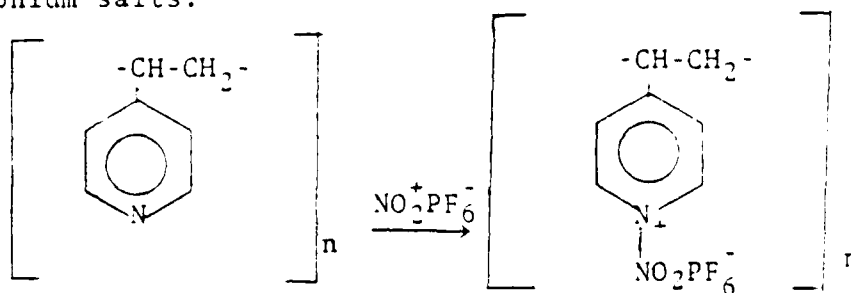
Polymer III was prepared via the following sequence:
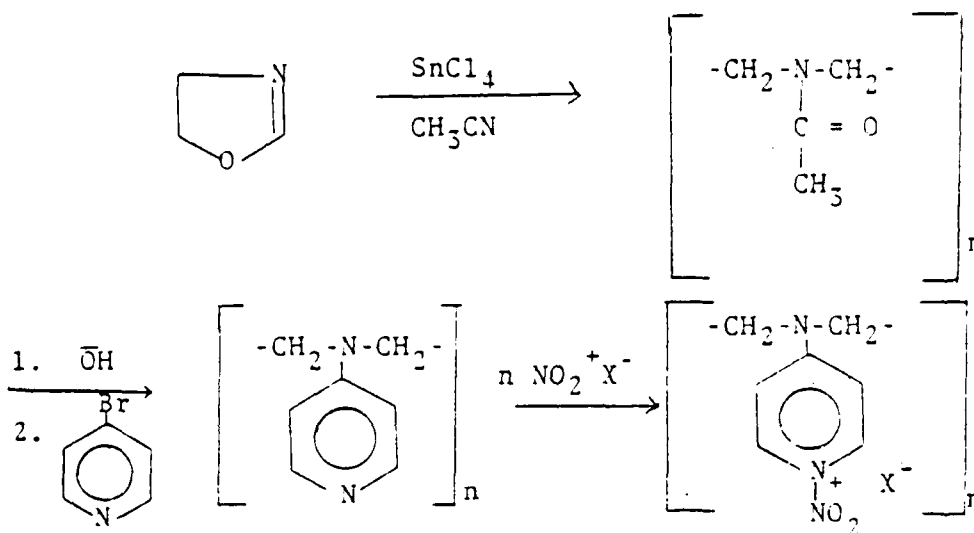
Polymers V and VI were prepared by reacting butylated polyethylene glycol and polyalkylylene sulfide with nitronium salts at -78°C. Polymers VII and VIII were prepared from the corresponding acid halides by reaction with silver nitrate.

Polymer II has been used as a reagent extensively during our initial studies because of the ease of its preparation. Aromatic substrates are nitrated rather clearly by this reagent in nitroethane solution.
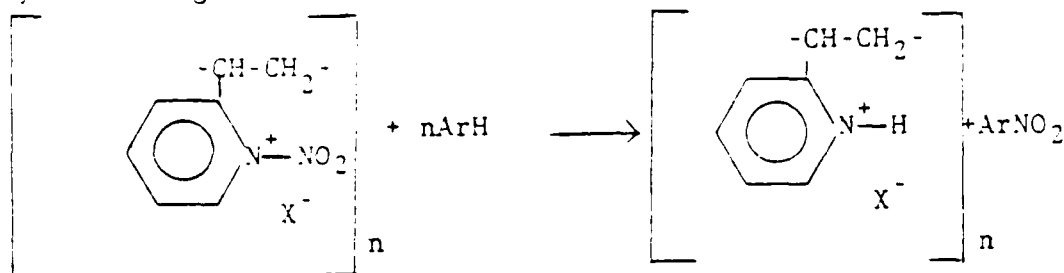
The nitrations therefore proceed under neutral conditions. With the linear polymer, the nitrations proceed under homogeneous conditions. With the cross linked (divinylbenzene) polymer, the heterogeneous nitrations provide rather interesting substrate selectivities. These are dependent upon the degree of crosslinking, the substrate selectivity being partially determined by the ability of the substrate to diffuse to the reaction site. This has been shown most dramatically by nitrating a mixture of benzene and anthracene. The relatively unrective benzene is nitrated preferentially in the presence of anthracene. The effect of polymer structure on substrate and positional selectivities allows one to design specific polymers in the form of microporous gels, macroporous beads, and membranes for selective nitrations.

The Three Phase Test has been applied to settle the question of mechanism of nitration by N-nitropyridinium salts. It has been suggested that the nitrations might proceed through predissociation followed by nitration of the substrate by the free nitronium ion. Our experiments with cross linked polymers indicate that the free nitronium ion is not involved in nitrations with N-nitropyridinium salts.

A column reactor has been constructed to carry out nitrations on a continuous basis. A solution of the nitronium salt through the column is followed by the passage of the aromatic substrate. The pyridinium polymer is then deprotonated with triethylamine and the cycle is repeated.

Interesting polymeric system have thus been developed to study mechanistic questions and to achieve substrate selectivities not obtainable under conventional conditions.

Polyethers as Complexing Agents for Reactive Cations.

The Crown Ether Complexed Nitronium Ion Nitratio of Toluene.

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ABSTRACT

The reactivity and selectivity of the nitronium ion in electrophilic aromatic substitutions are substantially altered by complexation with polyethers. Nitration of toluene with NO_2BF_4 complexed with 18-crown-6, 15-crown-5, 12-crown-4, and polyethylene oxide in several solvents at room temperature resulted in a reduction in meta substitution (0.6 -1.6% meta-nitrotoluene) over nitration without polyethers (2.5% meta-nitrotoluene). The ortho to para substitution ratios ranged from 1.45 to 2.44 depending on the solvent and polyether used. In competitive studies, crown ether - complexed NO_2BF_4 nitrated toluene 45-59 times faster than it nitrated benzene. This is the first reported case where ground state stabilization of the nitronium ion results in a substantial increase in both substrate and positional selectivity in toluene nitrations.

Dear Sir:

We wish to report that polyether complexation of reactive cations can substantially alter their reactivity. Specifically, we find that nitronium ions complexed with crown ethers show high substrate selectivity and substantially increased positional selectivity in the nitration of toluene compared to nitration with uncomplexed ions.[2,7,8]

Continued interest in nitrations stems not only from a theoretical standpoint[1-5] but from its considerable importance in industrial processes.[2] The first stage in the commercial production of toluene diisocyanates, a component of polyurethanes, is the two step dinitration of toluene. Only the 2,4- and the 2,6- dinitrotoluenes are needed; the 2,3- and 3,4- isomers, which are usually 4% of the total product, are wastes. The yield of unwanted isomers is controlled by the meta nitrotoluene generated in the first nitration step. Methods for altering positional selectivity in the mononitration of toluene has been the focus of substantial effort.[1-5,8] While some procedures are quite effective in changing the ratio of ortho to para substitution, reduction of meta substitution has been accomplished primarily by lowering the reaction temperature.[6,7,8] We sought a means to mimick "chemically" this temperature effect.

We envisioned that prior complexation of the nitronium ion, the active agent in most nitrations, would increase the effective activation energy and thus positional and substrate selectivity. A similar approach had been explored by Olah and co-workers[9] and by Cupas and Person[10] where alcohols, ethers, sulfides and substituted pyridines were used as complexing agents with NO_2BF_4. These increased substrate

selectivity substantially,[11] but they exerted only a marginal effect

upon positional selectivity in toluene nitrations.[12] Crown ethers

appeared attractive for complexation of the nitronium ion. Rod-like

with a diameter of ca. 0.27 nm,[13] the nitronium ion is well suited to the

cavity of 18-crown-6 (0.26-0.32 nm).[14] While crown ether complexation

of metallic cations and their use in activation of nucleophiles is well

documented,[15] there has been little investigation of the complexation

and modification of reactivity of non-metallic, electrophilic cations.[16]

Table 1 summarizes the nitration of toluene with NO_2BF_4 in the

presence of polyethers. These experiments were performed by the addition

of toluene in the indicated solvent to a solution of the preformed

polyether·NO_2^+ complex (0.2-0.5 M) under dry N_2. With 18-crown-6 in

CH_2Cl_2 the formation of the soluble nitronium ion complex was quite

rapid (1-2 min at 20°C). Without the crown ether NO_2BF_4 is essentially

insoluble in this solvent. Complex formation with 12-crown-4 was slower,

requiring 10 min for complete solublization, while with 15-crown-5 hours

were required for complete solublization. These complexes rapidly

nitrated toluene at room temperature with the liberation of HBF_4.[20]

The 18-crown-6 and 15-crown-5-nitronium complexes appeared to be quite

stable in solution and generally suffered very little decomposition

during the reaction.[21] Crystalline 18-crown-6 could be recovered

in 85% yield after nitration. The yields of mononitrotoluenes ranged

from 40-93%.[22]

Inspection of the results in Table 1 leads to several observations:

1. a substantial reduction in the amount of meta isomer was usually

produced in comparison with the corresponding control reaction without

added polyether; 2. both the open chain and the cyclic polyethers show this effect; 3. the ortho to para ratios change substantially with polyether and solvent; 4. when less polyether was used than required to completely solublize the NO_2BF_4, a substantial reduction in meta substitution still occurred,[25] and 5. CH_2Cl_2 is the best of the tested solvents for these nitrations.

If we assume Arrhenius behavior, then nitration with NO_2BF_4 in CH_2Cl_2 without added polyether (entry 1, Table 1) would have to be performed at -37°C, -50°C, and -65°C to achieve the reduction in meta isomer observed in the reactions at room temperature with added 15-crown-5 (entry 4), 18-crown-6 (entry 2) and 12-crown-4 (entry 5), respectively.[26] This represents a very rare occurrence where the reactivity of the nitronium is reduced substantially enough via a complexation (solvation) phenomena to show this magnitude of decreased meta substitution in toluene nitrations at room temperature.

Apparently, the rigid structure of the crown ethers is not necessary to obtain reasonable complexation and modified reactivity of nitronium ions. The use of polyethylene oxide (entry 9) and diglyme (entry 10) as complexing agents gave results similar to the crowns. The ability of polyethylene oxide to assume a crown-like conformation[27] in the complex probably results in a larger binding constant and accounts for the greater reduction in meta substitution compared to the digyme complex.

The factors influencing the isomer ratios are complex. The effect of the polyethers on the ortho/para substitution ratios are small compared to solvent effects (see entries, 1, 11 and 14, in Table 1). This is surprising in light of the presumably bulky nature of the polyether·NO_2^+

complexes. However, the stability constants and the topology of the complexes undoubtedly play a role in determining the extent of meta substitution. The 18-crown-6 and 12-crown-4 complexes, with larger stability constants[31] (vide infra), showed reduced meta substitution compared to the 15-crown-5 complex. The dicotomy between steric and electronic effects is exemplified by the two dicyclohexyl-18-crown-6 complexes (entries 7 and 8). Isomer A exhibits larger binding constants than isomer B with sodium, potassium, and cesium ions.[14,15] Here, isomer B shows the greater reduction in meta substitution.

To test the substrate selectivity of polyether complexed NO_2BF_4, a tenfold excess of a 1:1 mixture of benzene and toluene was nitrated with the soluble crown complexes in CH_2Cl_2.[28] These complexes showed substantially increased substrate selectivity over non-complexed NO_2BF_4[29] (Table 2). This increased substrate selectivity, coupled with the increased positional selectivity for the polyether complexed nitronium ions, is in accord with the reactivity-selectivity hypothesis of Stock and Brown.[30] The calculated ortho and para partial rate factors (Table 2) for the crown ether complexed NO_2BF_4 nitrations are the highest ever obtained for the nitration of toluene with any nitrating system at room temperature.

Conductometric titrations[31,32] of NO_2BF_4 with the crown ethers in CH_2Cl_2 showed the stoichiometry in the soluble complexes to be 0.92 ± 0.04 moles of 18-crown-6 per mole NO_2^+, and 3.0 ± 0.2 moles of 12-crown-4 per mole of NO_2^+. No well defined stoichiometry for the 15-crown-5 complex in CH_2Cl_2 was detected but our results indicate a minimum of 1.7 moles of 15-crown-5 are needed to solublize NO_2BF_4 in CH_2Cl_2.[33]

This nearly 1:1 stoichiometry of 18-crown-6 to NO_2^+ suggests that the nitronium ion might be symmetrically complexed in the cavity of the crown. A new highly polarized band appeared at 880 cm^{-1} in the Raman spectrum of the crown ether upon complexation with NO_2BF_4. This can been interpreted as arising from the symmetrical "breathing" mode of the ring in a highly symmetric complex in analogy with the K^+ complex of 18-crown-6.[34] Less than a 3 nm shift in the Raman symmetrical stretching frequency of NO_2^+ from 1408 cm^{-1} was noted upon complexation.[18] The infrared spectrum[35] of the complex with 18-crown-6 showed bands at 3770 cm^{-1}, 2383 cm^{-1}, and 540 cm^{-1} all characteristic of a linear nitronium ion.[35] The strong asymmetric stretching frequency at 2383 cm^{-1} of the complexed NO_2^+ is ca. 23 cm^{-1} above that of uncomplexed NO_2^+. In addition, a band appeared in the spectrum at 1669 cm^{-1} which might be due to another complexed form of the nitronium ion. [37] The infrared spectra of the 15-crown-5 and the 12-crown-4 complexes showed no bands in the 2340-2383 cm^{-1} region, but did show bands at 1640 cm^{-1} and 1638 cm^{-1}, respectively. In addition, the Raman spectra of the 15-crown-5 and the 12-crown-4 complexes showed no bands at or near 1400 cm^{-1}. Thus, a bent or unsymmetrically complexed form of the nitronium ion probably exists in these complexes.[37] This is consistent with the inability of the nitronium ion to fit into the cavity of these crowns.

The demonstration in this work that polyether complexation of the nitronium ion can alter its reactivity suggests that polyether complexation of other reactive electrophiles may prove valuable in changing selectivity and reactivity in other types of electrophilic processes. Further, the demonstration in both this work and others[28] that open chain polyethers exhibit complexation phenomena similar to the crown ethers opens the possibility of designing relatively cheap phase transfer agents for these reactions. We are currently investigating this possibility.

Table 1. Toluene Nitration with NO_2BF_4 in the Presence of Crown Ethers

Entry	Solvent	Temp.	Crown Ether	Crown(a) NO_2^+	Isomer Distribution (%)(b) ortho (±1.5)	meta (±0.2)	para (±1.5)	o/p(c) (±0.11)
1	CH_2Cl_2	23°C	none	(d)	59.2	2.5	38.2	1.55
2	CH_2Cl_2	21°C	18-crown-6	1.0(e)	61.7	0.8	37.4	1.65
3	CH_2Cl_2	23°C	18-crown-6	0.1(d)	59.1	1.4	39.5	1.50
4	CH_2Cl_2	20°C	15-crown-5	1.7(e)	58.4	1.4	40.1	1.45
5	CH_2Cl_2	23°C	12-crown-4	1.0(d)	59.8	0.6	39.6	1.51
6	CH_2Cl_2	20°C	12-crown-4	3.0	60.6	0.8	38.5	1.57
7	CH_2Cl_2	23°C	dicyclohexyl-(f) 18-crown-6(A)	1.0(e)	60.5	1.4	38.1	1.59
8	CH_2Cl_2	23°C	dicyclohexyl-(g) 18-crown-6(B)	1.0(e)	61.9	0.9	37.1	1.67
9	CH_2Cl_2	20°C	polyethylene oxide (h)		61.0	0.8	38.0	1.60
10	CH_2Cl_2	23°C	diglyme(i)	6.0(e)	59.4	1.4	39.2	1.51
11	SO_2	-10°C	none		63.2	2.5	34.3	1.84
12	SO_2	-10°C	18-crown-6	1.0(e)	66.8	1.3	31.8	2.10
13	SO_2	-10°C	18-crown-6	2.0	63.0	1.1	35.9	1.75
14	CH_3CN	22°C	none	-	67.8	2.3	29.8	2.27
15	CH_3CN	22°C	18-crown-6	1.0	69.7	1.6	28.6	2.44

(a) Mole ratio of crown ether to NO_2BF_4.   (b) Isomer distribution expressed as percent of total mononitrotoluenes as determined by gas chromatography. 24^2 Less than 2% dinitrotoluenes were produced in any run with crown ethers. (c) Ortho-nitrotoluene to para-nitrotoluene ratio.   (d) heterogeneous   (e) The minimum amount of polyether needed to make the solution homogeneous.   (f) cis-syn-cis-isomer (meso)   (g) cis-anti-cis-isomer (d,l)   (h) polyethylene oxide of 100 000 mol wt; used 1.80 g of polyether for 1.0 g of NO_2BF_4 (i) bis-(2-methoxyethyl) ether

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Table 2. Competitive Nitration of Benzene and Toluene with NO_2BF_4 Complexed with Crown Ethers in Dichloromethane at 23°C.

Crown Ether	Crown[a] NO_2^+	Benzene[b] NO_2^+	Toluene[b] NO_2^+	$\frac{k_T}{k_B}$ [c]	Partial Rate Factors f_o	f_m	f_p
18-crown-6	1.0	10	10	59	109	1.42	132
15-crown-5	1.7	10	10	56	98	2.35	134
12-crown-4	3.0	10	10	45	82	1.08	104
none		(d)	(d)	1.7(d)	3.27	0.14	3.18

(a) Mole ratio of crown ether to NO_2^+ used to make the NO_2BF_4 completely soluble in CH_2Cl_2.

(b) Mole ratio of benzene and toluene to NO_2^+ used. The solution of the complexed NO_2BF_4 in dichloromethane was added to a ten mole excess of a 1:1 mixture of benzene and toluene in CH_2Cl_2 with rapid stirring.

(c) Relative rate of toluene nitration to benzene nitration.[28]

(d) Taken from the work of G. A. Olah and N. A. Overchuk on nitrations with NO_2BF_4 in tetramethylene sulfone.[29] This ratio could not be determined in CH_2Cl_2 without added crown ether due to the insolubility of NO_2BF_4 in CH_2Cl_2. However, this number probably represents an upper limit for k_T/k_B in CH_2Cl_2.

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REFERENCES AND NOTES

1. P. B. D. De la Mare and J. H. Ridd "Aromatic Substitution, Nitration and Halogenation", Academic Press, Inc.: New York, N.Y. 1959.

2. "Industrial and Laboratory Nitrations", L. F. Albright and C. Hanson, eds., ACS Symposium Series 22, American Chemical Society, Washington, D.C., 1976.

3. J. G. Hoggett, R. B. Moodie, J. R. Penton and K. Schofield "Nitration and Aromatic Reactivity", Cambridge University Press: Cambridge, Great Britain, 1971.

4. William M. Weaver in "The Chemistry of the Nitro and Nitroso Groups", H. Fever, ed., Part II, Interscience Publishers: New York, N.Y., 1970.

5. B. V. Smith in "Organic Reaction Mechanisms", A. R. Butler and M. J. Perkins, eds., John Wiley and Sons: New York, N.Y., 1975, and references therein.

6. However, nitration of toluene with tetranitratotitanium(IV) in CCl_4 is reported to give only small amounts (0.5%) of meta product. R. G. Coombies and L. W. Russell, J.C.S. Perkin II, 1974, 830.

7. C. L. Coon, W. G. Blucher and M. E. Hill, J. Org. Chem., 1973, 38, 4243.

8. For an extensive compilation of toluene nitrations with many nitrating agents see G. A. Olah, "Fundamental Study of Toluene Nitration", U.S. NTIS, AD Rep., AD-A019273, 1976. Gov. Rep. Announce. Index (U.S.), 1976, 76, 152.

9. G. A. Olah, J. A. Olah, and N. A. Overchuk, J. Org. Chem., 1965, 30, 3373, H. C. Lin, Ph.D. Thesis, Case Western Reserve University, 1972; and ref 2, Ch. 1.

10. C. A. Cupas and R. L. Pearson, J. Am. Chem. Soc., 1968, 90, 4742.

11. Competitive nitrations of benzene and toluene mixtures at room temperature with these complexed nitronium ions nitrated toluene 2-44 times faster than benzene compared to 1.7 times with uncomplexed NO_2BF_4.

12. See ref. 2, Cha. 1, and ref. 8.

13. Estimated from the crystal structure of $NO_2^+NO_3^-$ (N_2O_5). Pár Emmanuel Grison, K. Eriks and J. L. de Vries, Acta Cryst., 1950, 3, 290.

14. "Synthetic Multidentate Macrocyclic Compounds", Reed M. Izatt and James J. Christensen, eds., Academic Press: New York, N.Y., 1978. See pp. 25, 217.

15. For some Reviews on crown ethers, see: C. J. Pedersen and H. K. Frensdorff, Angew. Chem. Internal Edit., 1972, 11, 16. J. J. Christensen, D. J. Eatough and R. M. Izatt, Chem. Reviews, 1974, 74, 351; G. W. Gokel and H. D. Durst, Synthesis, 1976, 168; and ref. 14.

16. While reports have appeared on the use of 18-crown-6 and its derivatives, as well as glymes, to stabilize aryldiazonium ions by complexation,[17,18] their use in altering the reactivity of electrophiles has not been generally explored. Recently they have been used as complexing agents for molecular bromine.[19]

17. R. M. Izatt, J. D. Lamb, B. E. Rossiter, N. E. Izatt, and J. J. Christensen, J.C.S. Chem. Comm., 1978, 386; and R. A. Bartsch and P. N. Terri, Tetrahedron Letts. 1979, 407; R. A. Bartsch, P. N. Juri, and M. A. Mills, ibid., 1979, 2503.

18. B. L. Haymore, J. A. Ibers, and D. W. Meek, <u>Inorganic Chemistry</u>, 1975, <u>14</u>, 541. The value of the $^-N\equiv N^+$ stretching frequency in the benzene diazonium cation increased by 32 cm^{-1} upon complexation with the cis-anti-cis isomer (B) of dicyclohexyl-18-crown-6.

19. K. H. Pannell and Armin Mayr, <u>J.C.S. Chem. Comm.</u> 1979 132.

20. The $HBF_4\cdot18$-crown-6 complex separates out of solution. Upon the addition of water to the nitration reaction using dicyclohexyl-18-crown-6 (isomer A, entry 7 in Table 1) a crystalline hydronium tetrafluoroborate·crown ether complex was isolated: mp 130.5-132.5°C, Calc. for $C_{20}H_{39}BF_4O_7$; %C: 50.25, %H: 8.16; found %C: 50.10, %H: 8.20 (Robutson Labs, Florham Park, NJ). For other hydronium ion-crown complexes see R. M. Izatt, B. L. Haymore, and J. J. Christensen, <u>J.C.S. Chem. Comm.</u>, 1972, 1308.

21. The 18-crown-6 and 15-crown-5 nitronium ion complexes in CH_2Cl_2 showed <i>no visible signs of decomposition after 3 weeks under</i> N_2 at room temperature. However, the 12-crown-4 complex gave a tar after this period of time. All of the crown ethers showed some decomposition with the liberated HBF_4 after extended periods of time.

22. These yields (GC) are corrected for the nitronium ion content of the NO_2BF_4 used in the experiments. The commercial samples of NO_2BF_4 that we used contained from 17% to 50% $NOBF_4$ as an impurity. Under our experimental conditions, $NOBF_4$ did not react with toluene. (see ref 23). The yields of mononitrotoluene with 18-crown-6 and 15-crown-5 complexed NO_2^+ were 88-93%, and with 12-crown-4 they were 40-60%. The low yields with 12-crown-4 are probably the result of some reaction of the crown ether with NO_2BF_4 (see ref. 21).

23. We were unsuccessful in obtaining NO_2BF_4 free of $NOBF_4$ from any commercial source. We subsequently prepared in our laboratory NO_2BF_4 free of $NOBF_4$. Our method of preparation and analysis will be published elsewhere.

24. Hewlett-Packard gas chromatograph model 5711A, 8% carbowax 20M on chromasorb W 80-100 mesh, 1.83 m x 2 mm glass column, 170°C, injector 200°C, detector 350°C, N_2 flow rate 30 mL/min, flame ionization detector; nitrobenzene 7.6 min, ortho-nitrotoluene 8.7 min, meta nitrotoluene 10.6 min, para-nitrotoluene 12.2 min. Dinitrotoluenes and crown ethers were analyzed by temperature programming 155° to 230° @16°/min. Yields were determined by internal standard (n-pentadecane).

25. The results from the runs that were heterogeneous are probably an average of cocomitant nitration from solubilized and solid NO_2BF_4.

26. This is not an unreasonable assumption since Coon, et al (ref. 7) obtained meta nitrotoluene in 0.53% at -60° and 1.08% at -30°C with nitronium trifluoromethanesulfonate in CH_2Cl_2.

27. H. Sato and Y. Kusumoto, Chemistry Letts., 1978, 635, and references therein.

28. For a discussion on the competitive method of nitration see M. J. S. Dewar, T. Mole, and E. W. T. Warford, J. Chem. Soc., 1956, 3576.

29. Competitive nitrations with uncomplexed NO_2BF_4 have been shown to be mixing controlled (see P. F. Christy, J. H. Ridd, and N. D. Stears, J. Chem. Soc. (B), 1970, 797). Thus, the ratio k_T/k_B of 1.7 for NO_2BF_4 nitration in tetramethylene sulfone may not be correct. Nonetheless, it's probably not much greater than this. G. A. Olah and N. A. Overchuck, Can. J. Chem., 1965, 43, 3279.

30. L. M. Stock and H. C. Brown, Adv. Phys. Org. Chem., 1963, 1, 35.

    The partial rate factors obtained for the crown ether·NO_2^+ nitrations

    fit the altered selectivity relationship, $\log p_f = -0.17 + 1.38$

    $\log (p_f/m_f)$, recently published by Santiago, Houk and Perrin

    (J. Am. Chem. Soc. 1979, 101, 1337) much better than nitrations with

    uncomplexed NO_2BF_4. In fact, complexation of NO_2BF_4 with the crown

    ethers nearly transforms the apparent anomalous reactivity vs.

    selectivity behavior of NO_2BF_4 in nitrations into normal behavior

   for an electrophilic process.

31. These titrations were performed on suspensions of greater than

    95% pure NO_2BF_4[23] in CH_2Cl_2 at 30°C under N_2 with incremental additions

    of crown ether. The conductivity increased linearly with each

    addition of crown ether until the end point was neared. The conductivity

    increased only slightly with further additions of crown ether after

    the end point was reached. The conductivities were measured using

    a dip-type conductivity cell (Yellow Springs Instrument Co.,

    model #3403). The final concentrations of the crown·NO_2^+ complexes

    were 0.02 M. From the shape of the curves the estimated stability

    constants for the 18-crown-6, 15-crown-5 and 12-crown-4 complexes

    in CH_2Cl_2 are approximately 10^5, $<10^2$, 10^3, respectively.

32. C. J. Pedersen and H. K. Frensdorff, Angew. Chem. Int.Ed. Engl.

    1972, 11, 16; D. A. Skoog and D. M. West, "Fundamentals of Analytical

    Chemistry", 2nd ed.; Holt, Rinehart and Winston, Inc.: New York,

    1969; p. 570.

33. The lack of a well defined stoichiometry for the complex indicates

    a relatively weak binding constant for 15-crown-5 and NO_2^+ in CH_2Cl_2.

    A repeat of the titration in sulfolane gave a curved titration

plot which showed no further change in conductivity after the mole ratio of added crown ether to NO_2^+ reached 1.45. (stability constant for the complex is probably $<10^3$.)

34. H. Sato and Y. Kusumoto, Chemistry Letts., 1978, 635, and references therein.

35. The infrared spectra were recorded as solutions in CH_2Cl_2 using AgCl windows and teflon spacers 0.01 mm thick.

36. D. Cook, S. J. Kuhn, G. A. Olah, J. Chem. Phys, 1960, 33, 1669, R. W. Sprague, A. B. Garrett and H. H. Sisler, J. Am. Chem. Soc. 1960, 82, 1059, R. Teranishi and J. C. Decius, J. Chem. Phys., 1954, 22, 896.

37. Here, the bands at 1669-1638 cm^{-1} in the crown ether complexes might arise from a $-NO_2$ antisymmetrical stretch in an oxonium type complex:
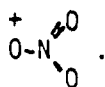
$$\overset{+}{O}-N\overset{\nearrow O}{\searrow_O} \;.$$

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A NEW STABLE AMINE NITRATE

Abstract

When the solid crystalline sulfate of 2,2-bis(aminomethyl)-1,3-diaminopropane is treated with excess nitric acid, the sulfate ion is displaced completely and the crystalline nitrate $C(CH_2NH_2) \cdot 4HNO_3$ can be isolated in 99% yield. This nitrate has some striking properties: (1) low solubility in water, (2) higher density than the more familiar amine nitrates, and (3) no melting or other phase changes in the range 25 – 200°C. The attractions of the tetramine $C(CH_2NH_2)_4$ as a precipitant for sulfuric and nitric acids will be presented.

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NITRATION VIA DIAZOTIZATION

by

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ABSTRACT

Many nitrogen heterocyclic compounds are
easily nitrated by converting the amino deriva-
tive to the diazonium salt and substituting with
nitrite ion with or without copper ion cata-
lyst. The preparation of 3,5-dinitro-1,2,4-tri-
azole, 5-nitrotetrazole, and attempts at prep-
aration of 3,6-dinitro-1,2,4,5-tetrazine will be
discussed.

THE TRINITRATION OF TRICHLOROBENZENE

Abstract

A parametric study of the nitration of trichlorobenzene (TCB) in nitric acid/oleum has been undertaken, with a view to optimising the production of 1,3,5-trichloro-2,4,6-trinitrobenzene (T3). It has been shown that under the conditions studied, efficient trinitration of TCB is always accompanied by the production of around 10% of 1,2,3,5-tetrachloro-4,6-dinitrobenzene (T4), an unwanted by-product. A mechanistic investigation of T4 formation has shown that chlorination arises as a result of ipso nitration of the intermediate trichlorodinitrobenzene. This study has further suggested a method by which product purity may be enhanced directly and subsequent recrystallisation avoided.

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NITRATION OF ETHANOLAMINES

A series of nitrato nitramines (alkyl NENA's)
was prepared by the chloride-catalyzed nitration of
alkyl substituted ethanolamines. Included are several
previously unreported members of this series, as well
as the closely related and well known explosive DINA
(a dinitrato nitramine). Properties of these compounds
will be reported.

New observations on this known and useful nitration
procedure will be discussed. Our results in terms of
yields, by-products, catalyst, and other factors will
be presented.

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HUMBERSIDE   COLLEGE   OF   HIGHER   EDUCATION

HULL, ENGLAND

Abstract

2,2',4,4',6,6' – Hexanitrostilbene (HNS) is a heat resistant explosive which
is also important as a crystal growth modifier for melt-cast TNT. This work
has studied the preparation of HNS by catalytic oxidation of TNT, to contribute
to an understanding of the mechanism involved.

A typical reaction is marked by several colour changes, from brown to purple
to red-brown then blue.   Visible and ^{1}HNMR spectroscopy, hydrogen–deuterium
exchange experiments and electrochemical methods have been used to identify
intermediates involved in the reaction.   The colours have been assigned to
a 3-σ-complex of TNT, the trinitrobenzyl anion, 3-σ- and 1-σ-complexes
of 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB) and the HNS radical anion respec-
tively.

A pathway for the oxidation reaction has been proposed which involves a
radical mechanism with electron transfer from the trinitrobenzyl anion to
an electron acceptor.

Electrochemical Generation of N_2O_5

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Abstract

The anodic oxidation of N_2O_4 in aqueous and anhydrous HNO_3 has been investigated by controlled-potential techniques and found to be an excellent method for the preparation of solutions of N_2O_5 in anhydrous HNO_3. The product solutions can be used directly for the nitrolysis and nitration of organic compounds. In this paper the details of the construction of the electrolytic cell and the electrolysis procedure, some aspects of the analytical methods, and the major characteristics of the reaction are presented.

Introduction

Solutions of dinitrogen pentoxide in various solvents have found use in a variety of nitration and nitrolysis reactions ([1],[2]). Traditional methods for the preparation of N_2O_5 are based on the dehydration of HNO_3 using phosphorous pentoxide ([3]), trifluoroacetic anhydride ([4]), or sulfur trioxide ([5]). Dinitrogen pentoxide can also be made by oxidation of N_2O_4 with ozone ([6]). However, a much older, and potentially more convenient method is the synthesis of the N_2O_5 by electrolytic oxidation of N_2O_4.

The electrochemical synthesis of N_2O_5 by anodic oxidation of N_2O_4 was first reported in a 1910 German patent ([7]) and then investigated again in 1948 by Zawadski and Bankowski ([8]). We have reexamined the reaction by means of modern controlled-potential techniques and found the process to be an unusually convenient method for the preparation of solutions of N_2O_5 in anhydrous HNO_3 ([9]). Among other characteristics, the desirable features of an electrosynthesis are (a) easy control of the electrolysis, including an indication of when the reaction is complete; (b) ease of separation of the product from the starting materials or side-reaction products, if any; and (c) preparation of the product in a solvent suitable for further reactions. The electrosynthesis of N_2O_5 meets all of these criteria.

Because the electrolysis is carried out at controlled potential using a potentiostat, and because the principal reaction occurs in a region of electrode potential where the solvent background current is low, the electrolysis current decays to a low value when the reaction is complete. The N_2O_4 is completely consumed, N_2O_5 is the only product, and no other species are introduced into the solution. The solutions of N_2O_5 in anhydrous HNO_3, which can be prepared with up to 25-30 wt.% N_2O_5, can be used directly in nitrolysis and nitration reactions. The anhydrous HNO_3, to which liquid N_2O_4 is added to prepare the starting solutions, can also be produced by electrolysis of reagent-grade red-fuming nitric acid. In this paper we outline the important aspects of the experimental procedure and describe some of the characteristics of the syntheses of N_2O_5. Additional details can be found in our earlier publication (9) and are available from the authors on request.

Experimental Procedures

Reagents. The initial solution for the electrolysis is a solution of N_2O_4 in anhydrous HNO_3 of about the same molarity as the desired final solution of N_2O_5. Anhydrous nitric acid can be prepared by distillation of a mixture of 90% HNO_3 (white fuming) and oleum at reduced pressure. Alternatively, the desired solution of N_2O_5 in anhydrous HNO_3 can be "bootstrapped" by first electrolyzing a sample of red fuming nitric acid. This acid, available as a reagent-grade chemical from MCB, consists of ~15% N_2O_4, ~2% H_2O, and the remainder HNO_3. The N_2O_5 formed by the electrolysis is consumed by the H_2O until an excess of N_2O_5 is present. By carrying the electrolysis to completion (low current), the resulting solution can be assayed accurately by NMR (see below) to determine the exact concentration of N_2O_5. Then N_2O_4 is added to the solution and oxidized to produce the desired final concentration of N_2O_5. N_2O_4 is available as a C.P. liquid in cylinders from Matheson and Air Products & Chemicals. Its boiling point is 21°C; transfer containers should be cooled in an ice bath, and solutions prepared on a weight basis.

Electrolysis Cell. For laboratory-scale batch preparations of N_2O_5, the cylindrical cell shown in Figure 1 is best because the control potential can be applied to the anode uniformly. Provision for cooling the cell solution to <20°C is desirable to avoid excessive loss of N_2O_4 from the
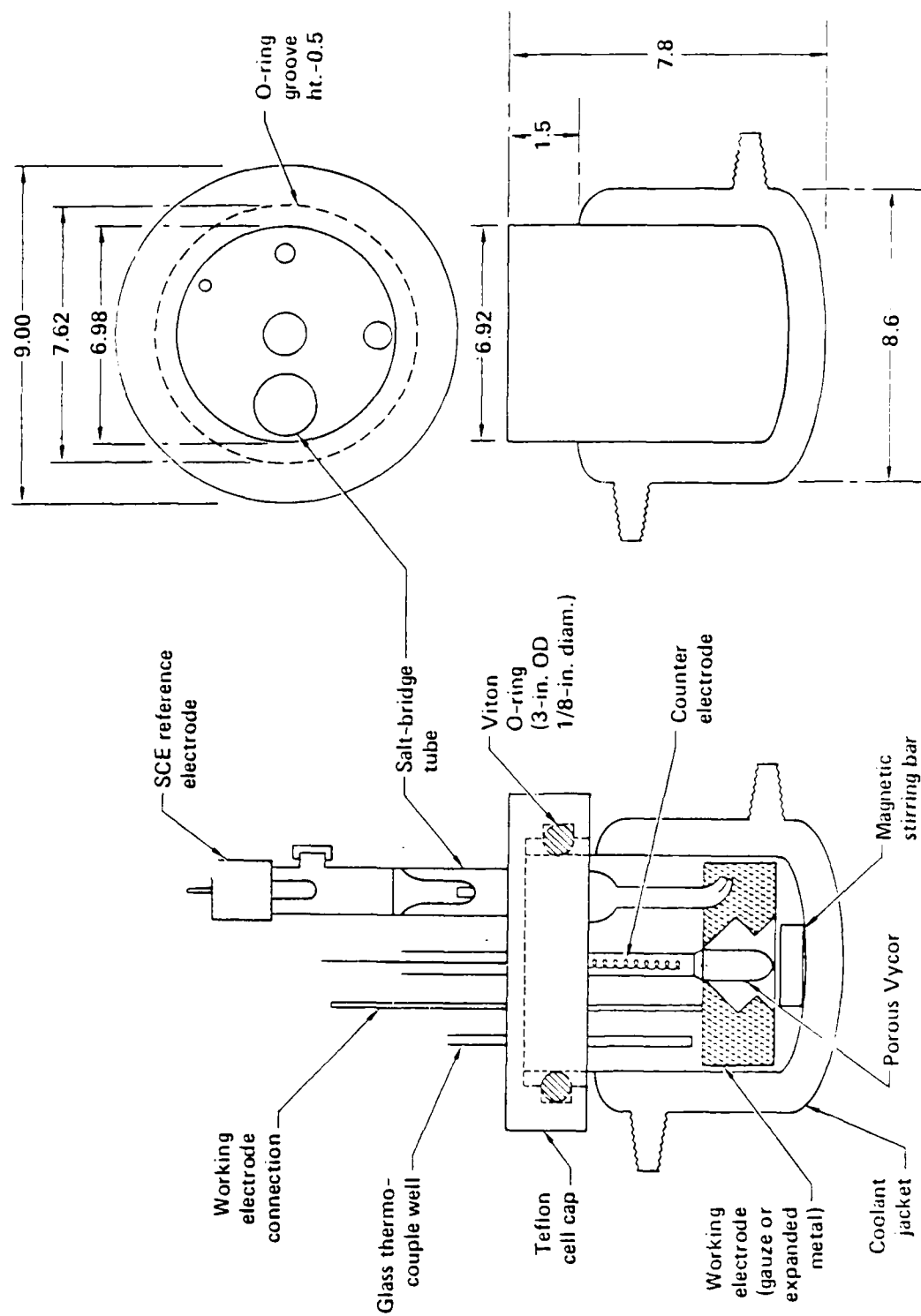
78

Figure 1. Glass electrolysis cell for electrosynthesis of N_2O_5. (Dimensions in cm. except as noted)

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anolyte and disruptive gas evolution from the catholyte. Stirring is important to ensure adequate heat transfer; however, solution mass transfer is not the rate-controlling step in the overall anodic reaction. Because of the electrocatalytic nature of the oxidation of N_2O_4 to N_2O_5, only certain anode materials are active, and the surface area of the anode determines the rate of the reaction. Thus the ratio of the area of the anode to the volume of the solution should be as large as possible.

For preparation of 125 mL volumes of N_2O_5/HNO_3 solution, we have used 45-mesh platinum gauze of ~125 cm^2 planar area, folded in a double thickness and into the shape of a cylinder. The reference electrode salt-bridge tube, which provides an additional liquid junction between the anolyte and the reference-electrode KCl solution, is an asbestos-fiber-tipped tube available from Perkin-Elmer (Coleman Instruments Div., Cat. No. 3-702 reference electrode reservior). The reference electrode is a miniature saturated-calomel electrode (SCE) available from Fisher Scientific Co. (Cat. No. 13-639-210). The various cell components are fitted into the holes in the cell cap by drilling the holes to exact size or by using Teflon tape.

One of the most important experimental aspects of this electrosynthesis is the choice of membrane to separate the anolyte from the catholyte. Our choice for the cylindrical cell is porous Vycor glass (Corning Glass No. 7930) because it is conveniently available in a cylindrical configuration, it is totally inert in the nitr icid/nitrogen-oxide media, and it maintains a low resistance to current flow. Teflon-based ion-exchange membranes have also been tested successfully, but are not as easily assembled with the proper geometry in the cylindrical cell.

We have used the porous Vycor in two forms: as a round-bottom tube, in which the upper section is ordinary Vycor (Fig. 1); or as a section of tubing mounted in a Kel-F holder. The latter design is shown schematically in Fig. 2; detailed dimensions and assembly instructions are available on request. The round-bottom tube must be fabricated by Corning glass. The tube shown in Fig. 2 is generally more convenient because it can be constructed in the user's laboratory from relatively inexpensive porous Vycor tubing obtained from Corning. Moreover, this porous section is easily replaced if broken or contaminated. Before use, new porous Vycor should be soaked in N,N-dimethylformamide, then water, and then dried in a desiccator. The cathode is a spiral of ~1-mm-diam. platinum wire (~5 cm^2 exposed to catholyte). Both the cathode and anode gauze should be boiled in 70% HNO_3 before initial use; subsequently, no cleaning is necessary.
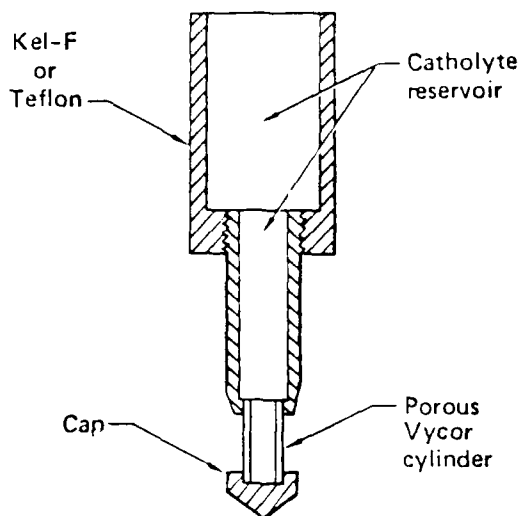
Figure 2. Catholyte compartment for N_2O_5 electrosyntnesis cell.

Instrumentation. For preparations of ~100 mL of 20% solutions of N_2O_5, the initial electrolysis current should be ~4 A in order to complete the electrolysis in <8 h. Cell voltages (anode to cathode voltages) will be <20 V when the membrane separator is functioning properly. Thus the output capability of the potentiostat that is used for this electrolysis should be about 5 A and 20 V. The anode-to-cathode voltage should be measured during the first electrolysis with a new cell assembly. A current integrator is not necessary, but provides an additional direct indication of the total quantity of electricity (and N_2O_4) consumed in the electrolysis. An electronic digital thermometer is very useful for monitoring the temperature of the anolyte. A circulating, constant-temperature cold bath or ice bath is used to cool the cell solution. If possible, this apparatus should be wired to regulate the temperature at the cell, rather than in the bath.

Electrolysis Procedure. If the electrolyses are carried out in a humid atmosphere, it is advisable not to circulate the cold coolant to the cell until after the anolyte solution is placed in the cell. Otherwise, moisture will condense on the inside of the cell, contaminate the anolyte, and decrease
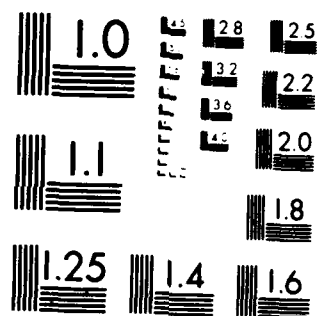
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the yield of N_2O_5. The cells we have used are open to the atmosphere during the electrolyses only through a small annulus where the anode connection passes through the cell cap. The cell is completely assembled prior to addition of the solutions; the anolyte is placed in the cell with a funnel or pipet through a port in the cell cap, then the port is immediately plugged with a piece of Teflon rod.

To conserve anhydrous HNO_3, the catholyte and the reference-electrode salt-bridge solutions may be aqueous HNO_3. The former solution may be 90% HNO_3 and the latter 70 or 90% HNO_3. Water is produced in the cathode reaction, thus the catholyte need not be anhydrous initially, and diffusion of water from the reference electrode assembly to the anolyte is negligible during the period of the electrolysis.

After placing the appropriate solutions in the cell compartments, closing the cell, inserting the reference electrode in the salt-bridge tube, starting the flow of coolant, making the electrical connections to the potentiostat, and starting the magnetic stirrer, the electrolysis is commenced. The control potential on the potentiostat is set initially to about +1.60 V vs. SCE to start the electrolysis at a lower current. If the electrolysis proceeds smoothly, the potential is then raised to the range of +1.85 to +1.95 V to effect the maximum current. If the anolyte temperature is not regulated at the cell, care must be taken that the temperature and electrolysis current do not "run away". This can occur because increasing solution temperature increases the current and this in turn increases the power dissipation and solution heating.

Because the current is limited primarily by the anode surface area, it will remain practically constant until a major fraction of the N_2O_4 has been electrolyzed. Then the current will decay rapidly to the background level. Typical electrolysis current behavior is shown in Fig. 6 of Reference 9. Electrolyses of 125-mL solutions of ~20 wt.% N_2O_4 with the cell of Fig. 1 will result in initial currents in the range of 3-4 A and background currents of 10-50 mA.

At the end of the electrolysis, after switching off the potentiostat, the N_2O_5-containing anolyte solution is removed from the cell and placed immediately in cold storage. The solutions are stable indefinitely at -80°C; they are also reasonably stable at ordinary refrigerator temperatures of +5°C. In a recent experiment in our laboratory, it was found that, starting with a 21 wt.% N_2O_5 solution, 98% of the original N_2O_5 remained after 6 days, and 94% after 21 days.

Solutions of N_2O_5 decompose with the evolution of O_2, thus they should not be stored in tightly-stoppered bottles. We have used glass-stoppered Erlenmeyer flasks sealed with Teflon sleeves or Kel-F grease.

Analytical Methods. Two different analytical methods have been investigated for the determination of N_2O_5 in anhydrous HNO_3 (9), and each has certain advantages and disadvantages. Raman spectroscopy has the advantage that most of the species present in these solutions can be seen in the spectra, particularly those from both N_2O_4 and N_2O_5. Dinitrogen tetroxide and dinitrogen pentoxide dissociate as follows (10):

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \tag{1}$$

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^- \tag{2}$$
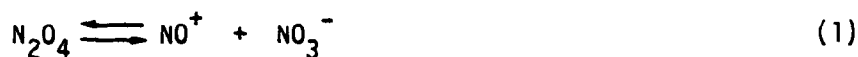
Instrumental variations require that the NO^+ and NO_2^+ peak heights be ratioed to that of HNO_3; preparation and maintenance of calibration standards is difficult; and the overall accuracy that can be achieved is probably about 5% (relative).

NMR spectrometry of the N_2O_5, based on a method developed by Happe and Whittaker (11), is capable of much better accuracy (1-2% relative). However, the NMR method involves measurement of the proton chemical shift resulting from the presence of NO_3^- ions in the anhydrous HNO_3, thus, as can be seen from equations (1) and (2), it is sensitive to both N_2O_4 and N_2O_5. The presence of 2 wt.% N_2O_4 in a mixture of N_2O_4 and N_2O_5 causes an error of ~1 wt.% in the measurement of the N_2O_5. Nevertheless, for the relatively pure solutions of N_2O_5 resulting from complete electrolyses, NMR is the preferred analytical method. The NMR analysis is calibrated using solutions of KNO_3 in anhydrous HNO_3. Because the electrolysis is quite predictable and reproducible after a few shakedown runs, NMR assays of the product solutions are not always necessary.

Characteristics of the N_2O_5 Synthesis

The preparation of N_2O_5 by electrooxidation of N_2O_4 has some interesting features that are not completely understood. Zawadski and Bankowski (7)

proposed for this process the overall reaction:

$$N_2O_4 + 2NO_3^- \longrightarrow 2N_2O_5 + 2e^- \tag{3}$$
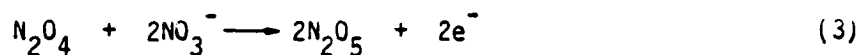
However, in our measurements of the N_2O_5 yield and product current efficiency, this stoichiometry has not actually been verified. When the porous Vycor membrane is used as a cell separator, the quantity of electricity consumed corresponds to 1.5 Faradays/mol N_2O_4 [vs. 2 in Eqn. 3)], the quantity of N_2O_5 produced corresponds to ~1.0 mol N_2O_5/mol N_2O_4 [vs. 2 in Eqn. (3)], and the product current efficiency is at best 67%.

It is known that several factors contribute to (1) the lower consumption of electricity than expected on the basis of the quantity of N_2O_4 taken, and (2) the lower than expected yield of N_2O_5. First of all, during the electrolysis, there is a flow of solution from the anode compartment to the cathode compartment by the process of electroosmosis. This amounts to 1-15% of the total volume of anolyte. Secondly, the cationic species that are present from the dissociation of N_2O_4 and N_2O_5, namely, NO^+ and NO_2^+, respectively (see Eqns. 1 and 2), migrate through the porous Vycor membrane toward the cathode and thus are lost as far as the synthesis is concerned. Recent experiments with ion-exchange membranes rather than porous Vycor as the cell separator indicate that these materials alter these transport effects in the electrolysis but do not significantly improve the yield of N_2O_5.

Another interesting aspect of the electrolysis is that if the control potential is changed or allowed to drift to more positive values, N_2O_5 will also be produced by oxidation of the solvent, HNO_3, via the reaction:

$$NO_3^- \longrightarrow NO_2^+ + \frac{1}{2} O_2 + 2e^- \tag{4}$$
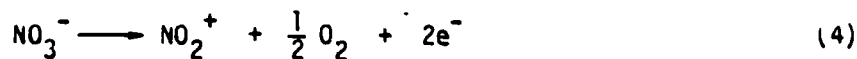
The product current yield is reduced, but the existence of this process relaxes the requirement for stringent potential control.

Conclusions

Although specialized equipment is required for the electrosynthesis of N_2O_5, once it is implemented, the electrolyses are quite straightforward to carry out. The N_2O_5/HNO_3 solutions produced are free from dehydrating reagents, are relatively stable at refrigerator temperatures, and are easy to handle in reactions with organic compounds.

Acknowledgements

References

1. L. F. Fieser and M. Feiser, Reagents for Organic Synthesis, J. Wiley, New York, Vol. 1, 1967, pp. 322-324.

2. K. Schofield, Aromatic Nitration, Cambridge University Press, Cambridge, 1980, pp. 73-76.

3. T. E. Stevens and W. D. Emmons, J. Amer. Chem. Soc., 79, 6008 (1957).

4. J. H. Robson, J. Amer. Chem. Soc., 77, 107 (1955).

5. German Patent No. 871,744 (1938).

6. A. D. Harris, J. G. Trebellas, and H. B. Jonassen, in Inorganic Syntheses, McGraw-Hill, New York, Vol. IX, p. 83, 1967.

7. German Patent No. 231,546 (1910).

8. J. Zawadski and A. Bankowski, Roznicki Chem., 22, 233 (1948).

9. J. E. Harrar and R. K. Pearson, J. Electrochem. Soc., 130, 108 (1983).

10. C. C. Addison, Chem. Rev., 80, 21 (1980).

11. J. A. Happe and A. G. Whittaker, J. Chem. Phys., 30, 417 (1959).

SYNTHESIS OF POLYNITRO AROMATICS

To be presented at
INTERNATIONAL CONFERENCE ON NITRATION
at SRI International
Menlo Park, California
27-29 July 1983

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ABSTRACT

For some time we have been studying new methods of synthesizing
polynitroaromatics. It is known that direct nitration of aromatics
introduces a limited number of nitro groups into an aromatic ring. A
new method of oxidation of an amino group to nitro, which employs a sul-
furic acid solution of peroxydisulfuric acid, has enabled us to synthe-
size many new polynitroaromatic compounds, including hexanitrobenzene.
Our recent efforts directed towards synthesis of various new polynitro-
aromatics will be discussed.

Our interest in polynitroaromatics is a part of our larger effort
to synthesize new nitrocarbons. Nitrocarbons may be described as
compounds composed only of nitro groups attached to carbon at the
nitrogen atom. They represent a rather small group of substances. The
first to be prepared was tetranitromethane obtained by Shiskov in 1861.
Not until 53 years later was the second nitrocarbon described—
hexanitroethane synthesized by Will and reported in 1914. About another
50 years later, in 1966, the third nitrocarbon, hexanitrobenzene was the
subject of an X-ray crystallographic study by Akopyan and coworkers and
reported in the Soviet literature. Other physical data, including ^{13}C

NMR, were subsequently reported, but nothing on its method of preparation until our report which first appeared in 1979. Recently Baum and Griffin described experiments whereby tetranitroethylene could be generated in situ and trapped as its anthracene adduct. This adduct on heating loses nitrogen tetroxide to form the dinitroacetylene adduct. Also, recently we have synthesized decanitrobiphenyl which will be described in this report.

The first nitrocarbon of the aromatic series to be prepared was hexanitrobenzene. Our method of synthesis involves a simple peroxydisulfuric acid oxidation of pentanitroaniline in oleum or 100% H_2SO_4. The method is a general one for synthesis of polynitroaromatics and was used by us for the first reported synthesis of pentanitrobenzene. Hexanitrobenzene is a powerful explosive. It melts near 250° and may be sublimed under reduced pressure. Hexanitrobenzene is quite reactive toward nucleophiles. Heating with aqueous sodium hydroxide at 75° for 25 minutes, followed by acidification, produces trinitrophloroglucinol in quantitative yield. Similarly, reaction of hexanitrobenzene in benzene solution with ammonia gas gives triaminotrinitrobenzene in 95% yield.

Hexanitrobenzene undergoes an interesting reaction with hydrogen halides, either anhydrous in benzene solvents or concentrated aqueous solution. Only one nitro group is displaced leading to pentanitro-chloro-, bromo-, or iodobenzene usually in high yield. Reaction conditions could not be found whereby more than one halogen could be introduced without decomposition of reactants. Hydrogen fluoride failed to undergo the reaction. Pentanitrobenzene also undergoes the reaction

leading to a tetranitrohalobenzene with meta substitution. 1,2,3,5-
Tetranitrobenzene reacts, but more slowly. Soviet workers have recently
reported similar reactions of pentanitroaniline and tetranitrophenol,
again with mono halogen substitution.

A second aromatic nitrocarbon has been prepared in our laboratory—
decanitrobiphenyl. Its properties are similar to those of hexanitro-
benzene, although decanitrobiphenyl is somewhat less stable on storage
at room temperature. It may be prepared in 7 steps from 4-chlorobenzoic
acid. Nitration provides 4-chloro-3,5-dinitrobenzoic acid in high
yield. Methyl 4-chloro-3,5-dinitrobenzoate was employed in the Ullman
coupling to the desired biphenyl diester. The required 2,2',6,6'-tetra-
nitrobenzidine was synthesized by Schmidt conversion of the precursor
diacid to the diamine, a very efficient, nearly quantitative reaction
which is much superior to the Curtius or Hofmann reactions which give
lower yields.

The nitration of 2,2',6,6'-tetranitrobenzidine to octanitrobenzi-
dinene is conducted in mixed acid at about 70° using 15-20 mole-
equivalents of nitric acid. The total acid concentration is quite
critical in this nitration. The maximum yields of around 70% were
obtained at total acid concentration of 98-99%. The yield drops sharply
outside this acid concentration range. The oxidation of the diamine to
decanitrobiphenyl was performed using peroxydisulfuric acid in oleum;
the best yields of 35-40% were obtained in 30% oleum. The oxidation is
quite slow relative to other oxidations of this type. The compound is
isolated as yellow prisms melting at 245°C. It is difficult to purify

owing to its reactivity towards solvents which results in its decomposition. It reacts with sodium hydroxide or ammonia as does hexanitrobenzene, but the products are not crystalline.

We have initiated studies of the synthesis of polynitronaphthalenes, including octanitronaphthalene. Of the many possible polynitronaphthalenes, none have been synthesized containing more than four nitro groups. One important precursor is 3,7-diamino-1,5-dinitronaphthalene. Oxidation of 2,6-dimethylnaphthalene with aqueous dichromate at 250°C provides an excellent yield of naphthalene-2,6-dicarboxylic acid. The diacid may be nitrated with concentrated nitric acid to the 4,8-dinitrodiacid in 65% yield. The Schmidt reaction very efficiently converts the dinitrodiacid to the desired 3,7-diamino-1,5-dinitronaphthalene in quantitative yield.

The conversion of 3,7-diamino-1,5-dinitronaphthalene to the corresponding tetranitro derivative could not be achieved by direct nitration. The bistrifluoroacetamido derivative, however, was readily nitrated at the remaining peri positions to form a tetranitro derivative. Deacylation occurred cleanly in methanolic HCl to provide the desired 2,6-diamino-1,4,5,8-tetranitronaphthalene. This reaction sequence was not successful with the acetyl derivative, however; the principal nitration product was the trinitro derivative. The tetranitrodiamine or its bistrifluoroacetamide could not be further nitrated without destruction of the naphthalene ring. To obtain polynitronaphthalene derivatives requires a very carefully controlled substitution sequence.

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2,6-Diamino-1,4,5,8-tetranitronaphthalene was designed for further
nitration to 2,6-diamino-1,3,4,5,7,8-hexanitronaphthalene. Nitrations
of aromatic amines of this type often proceed via nitramine intermedi-
ates. We have isolated the bisnitramine, 2,6-diamino-N,N',1,4,5,8-hexa-
nitronaphthalene, using 80% H_2SO_4/100% HNO_3 (100 equivalents) at 3°C.
Rearrangement of the nitramino groups would ordinarily occur into the
ortho positions leading to the desired hexanitrodiaminonaphthalene;
oxidation of the latter would produce octanitronaphthalene. However, it
is known that nitramine rearrangements to C-nitro products become slow
in aromatic rings containing many electronegative substituents. Instead
of formation of a hexanitrodiaminonaphthalene in acid medium we observed
a different rearrangement leading to a product believed to be a diazo
oxide, a sensitive energetic explosive compound. We frequently find
rearrangements of this type to occur in nitration of other polynitro
aromatic amines which we have investigated.

Our experiments in the area of polynitroaromatic synthesis have
resulted in some new synthetic methods and some new chemistry unique to
these substances.

POLYNITROPOLYHEDRANES

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ABSTRACT

The objective of this program is the preparation of stable polynitro compounds
of high density. Calculations of bond strength, and a review of the literature, sug-
gested that nitrated three-dimensional polyhedranes would be of interest. Accordingly,
compounds of this type have been prepared on a preliminary basis, as follows: 1,4-di-
nitrocubane (P.E. Eaten et al, in press); 1,3,5,7-tetranitroadamantane (G. P. Sollott,
E. E. Gilbert, J. Org. Chem. 45, 5405 (1980); 1,3,5,7-tetranitratoadamantane (E. E.
Gilbert, unpublished). Their properties are encouraging, and further work is in
progress toward more highly nitrated derivatives of these and other materials. Sev-
eral synthetic approaches are being considered, including variations of established
multistep syntheses and direce nitration of rhe hydrocarbons.

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electron transfer	kinetics	electrochemical	
lower nitrogen oxides	mixed acid	polynitroaromatics	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

In July, 1983, a 2 1/2 day meeting on nitration chemistry was held at SRI International in Menlo Park, CA. The sponsors of the meeting were ARO and AFOSR, and 24 papers on the various aspects of nitration were presented. The 71 attendees heard presentations on the mechanism of aromatic nitration, including discussions of the possible participation of electron transfer, and advanced studies in ipso nitration. Also included were presentations of poly-nitroaromatics and polynitropolyhedranes

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